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Blue Shade Hues:
A Study of Blue Pigments Used by
Romano-British Wall-Painters

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ABSTRACT

Following an earlier study of different coloured pigments used in Roman wall-plaster paintings, this research project investigates the use of the synthetic pigment commonly known as Egyptian Blue in Romano-British wall-plaster paintings. Samples of Egyptian Blue pellets were obtained from excavations at the Romano-British sites of Fishbourne Roman Palace, near Chichester, Piddington near Northampton, Turners Hall Farm, near St Albans, and from excavations at Verulamium (Roman St Albans).

The aim of this study is to determine the chemical composition, fabric and texture of each pellet as well as attempting a textural and geochemical classification of the pellets, using well established analytical techniques, particularly LA-ICP-MS and SEM-EDAX. The colour of the pellets was examined and identified using the *Munsell Book of Color (Matte Finish Collection)* 1973. The results of the analysis of the Egyptian Blue pellets found on Romano-British sites showed that differing amounts of silica, copper, calcium, as well as smaller amounts of other elements, were used in their manufacture. Most of the pellets examined appear to have been manufactured locally, though some were almost certainly imported.

Experimental work was undertaken, both in the laboratory and out in-the-field where a reconstructed Bronze Age Clamp Kiln and an Iron Age Belgic Kiln were used, to reproduce the synthetic pigment Egyptian Blue, using a recipe similar to that used by earlier investigators. Such recently manufactured Egyptian Blue pellets were applied, as a pigment, to damp lime mortar, in an attempt to correlate the achieved colour with the firing time.

Similar techniques were used in an attempt to ascertain the nature of the pigments used on the small fragments of painted wall-plaster found in a back filled trench, from Wheeler's 1930 - 33 excavations at Verulamium. On two of the fragments gas chromatographic analysis was applied to determine the nature of the binding material that might have been used.

This study is thought to be the first in-depth investigation of Romano-British Egyptian Blue pellets and thereby contributes to the art history and archaeological knowledge of this period.

CHAPTER 1

Introduction

*Pigments ... have been explored by painters since the beginnings of art
and by scientists for many generations*

Gettens & Stout, 1966, 140

1.1 Preliminaries

The word pigment (Latin *pigmentum*) describes a material or substance that may be used as a colouring agent. The word ‘colour’ cannot itself describe a material substance, for colour is only a luminous sensation resulting from the selective absorption of certain wavelengths of light. From the electromagnetic energy emitted by the sun, the human eye can only detect as light, energy within the visible spectrum, that is, energy with radiation wavelengths in the range of approximately 4000Å to 7000Å.* (Skoog & Leary, 1992, 89). This visible portion of the electromagnetic or solar spectrum is, by custom, referred to as ‘colour’.

The word ‘pigment’ is thus used for a colouring substance, which is usually made ready for use in the form of a dry powder. Such pigments, whether crystalline or amorphous, were ground to fine particles which, as they have no adhesive qualities of their own, require to be mixed with a binding agent or medium to hold them *in situ*, and the combination constitutes what is known as a ‘paint’. Pigments may be divided into different categories such as mineral or organic and natural or artificial, depending on their origin.

* 1 Ångstrom unit = 10^{-10} m. (thus, 10Å = 1nm).

Natural mineral pigments are found in the earth in the form of carbonates, sulphates, sulphides and oxides. Ochres are natural earth pigments consisting of clay and silica, often with different concentrations of iron. In ancient times after extraction the mineral was left to dry and was then roughly ground and sieved to remove any impurities, then re-ground to a fine powder, cleaned and dried. Organic pigments are commonly obtained by maceration of fruits, leaves, bark, and the roots of plants. Once macerated the ‘mush’ is boiled and the coloured pigment finally obtained by evaporation and desiccation (Mora & Philippot, 1984). Some artificial pigments are produced by well defined chemical processes whereby they are obtained by sublimation; alternatively they may be produced by precipitation of chemical solutions. Other artificial pigments, Egyptian Blue being a classic example, are produced by a complex operation involving the fusing together of different compounds at a high temperature.

In earlier studies the term ‘blue frit’ was used to describe the calcium-copper-tetrasilicate mineral, cuprorivaite, $\text{CaCuSi}_4\text{O}_{10}$, produced by mixing and firing together silica, copper and calcium compounds, normally with a flux. In describing a range of vitreous materials, Tite (1987) uses the term *frit* to describe a ... *sintered, polycrystalline material* ... However, the term *frit* is now, conventionally, restricted to the description of amorphous glass-like materials that demonstrate no crystalline structure. Thus, what was formally known as *blue frit* is today known as ‘Egyptian Blue’: the term is used to describe crystals of the mineral cuprorivaite; it is also used to describe smaller and larger quantities of a multiphase material, the bulk of which is composed of cuprorivaite, though several other phases, including glass, are also, invariably, present.

1.2 Historical background

Over many millennia modern man has produced paintings of various forms and shapes by applying coloured pigments to hard, smooth surfaces. Painting, unlike other more ephemeral art forms, such as music and dance, was probably one of the earliest ways in which man sought to express his own personality and his emerging belief in and understanding of, a possible existence beyond the material world.

It was during the third millennium BC that the Egyptian artisans perfected the manufacture of the first known synthetic pigment, using silica, copper and calcium to produce what is now known as Egyptian Blue. The earliest known evidence for the use of this pigment was found in Egypt as early as the Fourth-Dynasty (*ca.* 2613 - 2494 BC) where it was formed into small objects such as cylinder seals, statuettes, amulets, inlays and beads (Lucas & Harris, 1962); at a slightly later date it was ground and used as a pigment on limestone sculptures and sarcophagi, wood, plaster and papyrus. From this time onwards Egyptian Blue became one of the most popular pigments used in Egyptian art (a fine example is shown in figure 1a); its use continuing into the Ptolemaic Period (4th century BC) and subsequently when it was in use throughout the Late Period into Greco-Roman times, 332 - 395 AD, (Chase, 1971 & Riederer, 1997). The term for Egyptian Blue in ancient Egyptian texts is *hšbd-iry* which is said to be an expression for the colour of lapis lazuli and also to signify that it is a synthetic product.

The manufacture of Egyptian Blue in Egypt, became a ... *resounding success* ... it was manufactured in large quantities and ... *was exported* ... across to the known Mediterranean world (Delamare and Guineau, 1999,

22). During the third and second millennia BC the art of wall painting was introduced to the Aegean islands of Thera, now known as Santorini, and Crete by peoples from the Eastern Mediterranean such as the Syrians and Egyptians (Doumas, 1992). The Aegean artists appear to have used two kinds of blue pigment, *viz.* azurite and the artificially produced Egyptian Blue (Doumas, 1992). It was during the period 1600 - 450 BC that the technique of wall painting was developed in metropolitan Greece following its cultural diffusion from the islands of Crete and Thera (Myers, 1967).

The Etruscans has close contacts with the inhabitants of the major Greek speaking areas to the south of their homeland in northern Italy and would have learnt about the use of Egyptian Blue from these contacts. The use of Egyptian Blue in Etruscan wall paintings is mentioned by Spurrell (1895) and their artists may have used Egyptian Blue in tomb paintings during the fourth and sixth century BC (Pontrandolfo *et al.*, 2004).

Use of Egyptian Blue is likely to have found its way into Italy, via trade links: Rome came into contact with both Greek and Etruscan art during the 6th century BC. Greek artists, such as Nicias and Aristolaus, began to flock towards Rome, as the city offered the best and most consistent source of patronage (Pliny, Book XXXV).

There have been numerous records of Egyptian Blue, found in relatively large amounts, in the so-called colour shops of Pompeii and in the tombs of Roman painters. In a tomb found in St Médard-des-Prés in France eighty samples of Egyptian Blue were found in wooden and bronze containers together with different kinds of tools used to apply the pigment to the prepared walls (Riederer, 1997). Towards the end of the fourth

century AD Roman artists had perfected the technique of wall-plaster painting using bold and vivid colours, especially the colour blue, in their paintings, see figure 1b. Their achievements influenced many of the latter-day fresco artists and will undoubtedly continue to capture the imagination of future generations (Mora & Philippot, 1984).

The study of Roman Britain wall-paintings has been mainly based on establishing a chronological order of the paintings (Davey & Ling, 1982) similar to those established by the German scholar August Mau's classification of the different 'styles' found in the Campanian cities of Pompeii and Herculaneum, and in Rome (Ling, 1992). Study of the nature of the pigments used on Roman Britain wall-paintings have been limited mainly to the different ochre colours (Davey & Ling, 1982). There is little published material on the blue pigments used in Romano-Britain, despite their archaeological importance. This view was confirmed by English Heritage and the National Trust (personal communications, 2008). In contrast, detailed investigations into Egyptian Blue pellets found on various Egyptian, Mediterranean and other sites has been on-going for many years: Spurrell and Russell in the 1800s and Laurie, Tite and Chase in the 1900s, to mention only a few of the early investigators.

The description of the historical use of Egyptian Blue in this Introduction is necessarily limited since a more comprehensive, chronological study of the use of this (synthetic) pigment is provided in the Literature Review, Chapter 2.

1.3 Objectives

The aim of this research project is to attempt to close the knowledge gap within this area of Romano-British archaeology by analysing and characterising fragments of blue (and green) painted plaster and Egyptian Blue pellets found on various archaeological sites, using well established analytical techniques such as LA-ICP-MS, SEM-EDAX and XRD, and via these techniques to determine the source, composition and formulation method(s) of the Egyptian Blue pellets used.

Specific study objectives are given below:

1. To determine the chemical composition, fabric and texture of the Egyptian Blue pellets reviewed from various Romano-British sites across the southern and central England (*viz.* Fishbourne Roman Palace, Piddington Roman Villa and two sites near modern day St Albans), as well as to attempt a textural and geochemical classification using well defined analytical techniques;
2. To establish the nature of other blue producing materials employed as a pigment on Romano-British wall paintings;
3. To improve the understanding of how Egyptian Blue pellets were manufactured by using experimental work, both in the laboratory and in field studies, using materials and techniques which are similar to those found to have been used by the artists working in Roman Britain;
4. To attempt to establish what type of binding material was used on two fragments of painted plaster from Verulamium.

The archaeological sites referred to and used as the source of archaeological material in this study are shown on Map 1.

This thesis has the following structure:

- Chapter 1 is an introduction with a general history of the use of Egyptian Blue;
- Chapter 2 reviews the available literature looking at the production, use and identification of Egyptian Blue (and other blue pigments) at various historical sites;
- Chapter 3 - Methodology – presents the use of different microscopic and geochemical techniques in order to establish the composition of Romano-British samples of blue pigments;
- Chapter 4 contains an analysis of Egyptian Blue pellets found at Fishbourne Roman Palace in order to determine the materials used in their manufacture. An attempt is made to ascertain whether or not the Egyptian Blue pellets found at Fishbourne were manufactured on site or were imported by the interior decorators/painters. The same analytical methods were applied to the Egyptian Blue pellets obtained from Piddington Roman Villa (Chapter 5), Turners Hall Farm (Chapter 6) and Verulamium (Chapter 7);
- Chapter 8 analyses and characterizes samples of blue (and green) pigments found on painted fragments located in the back-

fill from one of Mortimer Wheeler's trenches after the excavation (1930 - 33) of a high-status town house, found in 'Roman' St Albans. An attempt is also made to identify the type of binding material(s) used with two of the painted fragments.

- Chapter 9 presents the results of experimental archaeological activity, both laboratory and field-based, to investigate the manufacture of Egyptian Blue pellets using compositional data drawn from earlier Chapters and simulated ancient techniques; and finally
- Chapter 10 presents conclusions and suggestions for further work.

The structure of this thesis reflects the nature of the investigations undertaken. It initially focuses on the Egyptian Blue pellets found at different Romano-British sites (Chapters 4 - 7), then examines other blue materials that might have been employed as pigments (Chapter 8), and culminates in experimental work, using simulated ancient technologies, to examine the production techniques that were thought to have been used by the employed artisans (Chapter 9).



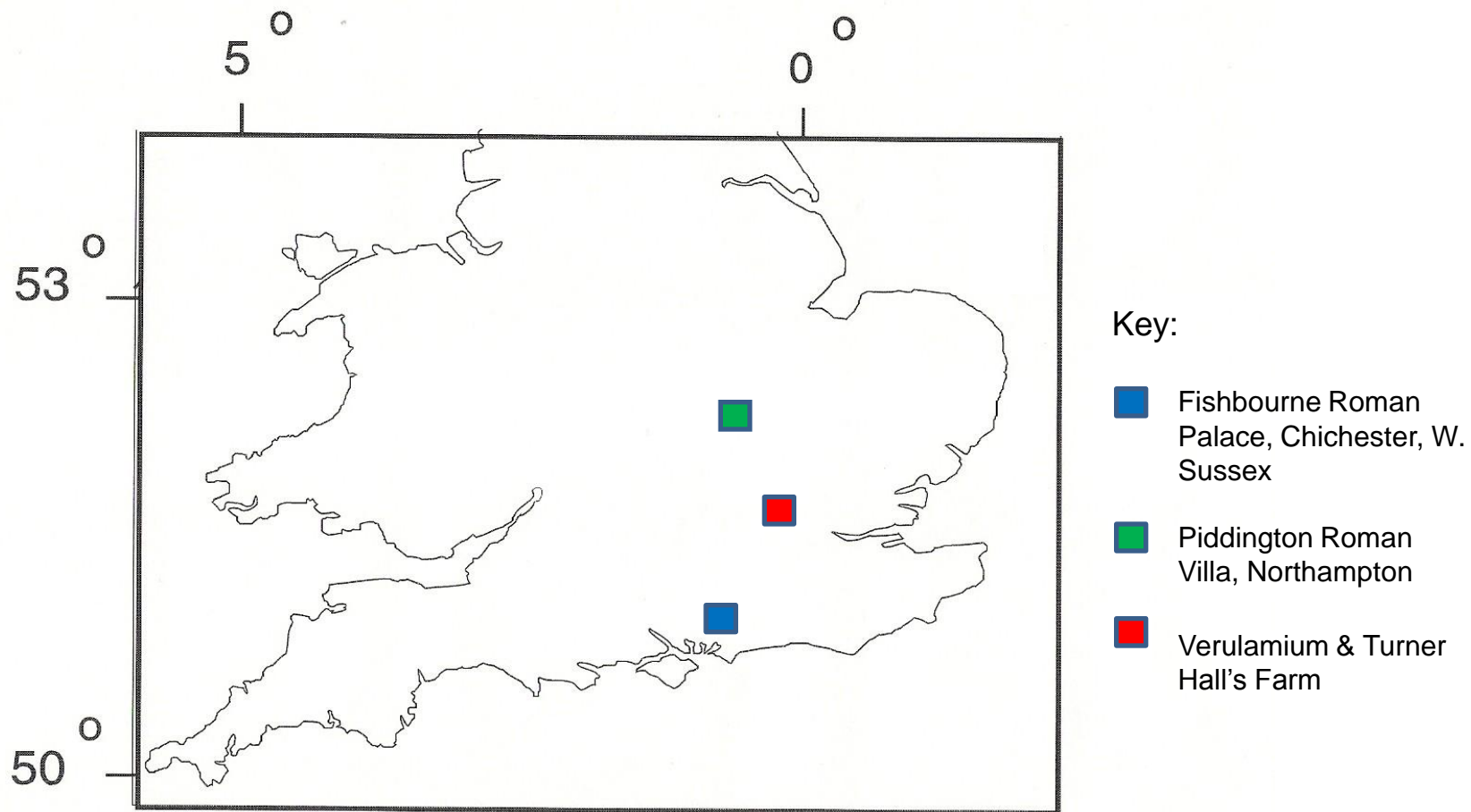
Figure 1a Blue pigment seen in a side chapel at Queen Hatchepsut's temple in the Valley of the Queens, Egypt (18th Dynasty)

Picture taken by the author



Figure 1b A detailed painting clearly showing the use of a blue pigment of Apollo playing the lyre, Palatine Museum, Rome.

Picture taken by the author



Map 1: Locations of archaeological sites discussed in this thesis (latitude and longitude marked).

CHAPTER 2

Literature Review

Reading is to the mind what exercise is to the body.

Richard Steele 1672-1729: The Tatler 18th March 1710

2.1 Introduction

Prior to undertaking this research project English Heritage, local archaeological societies, the National Trust and the Museum of London were contacted, to see if previous in-depth research had been undertaken, or was on-going, into Egyptian Blue or any other blue pigment used in wall-plaster paintings found on Romano-British sites. In all cases the answer was negative. A preliminary literature review (of archaeological material) was carried out by the author at the request of the recently retired chief executive of Sussex Archaeological Society and the recently retired Director of Fishbourne Roman Palace. This review indicated a paucity of material specific to Romano-British sites, despite a not insignificant number of relevant archaeological finds.

The main emphasis of contemporary research into Romano-British use of Egyptian Blue is directed towards laboratory experimentation. Very little work is aimed at exploring the nature of extant historic samples or investigating the materials and methods that might have been used by the ancient artisans operating in the British Isles.

This study makes a contribution towards a better understanding of some of the Egyptian Blue pellets found at a small number of Romano-British sites and also attempts to investigate the processes that might have been involved in the

manufacture of the pellets at these sites by using technologies that attempt to mimic those that might have been used by early artisans.

2.2 The Occurrence and Use of Egyptian Blue in Egypt.

According to Hatton and colleagues (2008, 1591) the ... *earliest surviving use of Egyptian Blue ... [in Egypt] ... was possibly in the painting from Tomb 3121 at Saqqara ... dated to the reign of Ka-sen who was the last king of the 1st Dynasty (ie circa 2900 BC).* In the same paper they also state (page 1591) that the use in Egypt of the pigment Egyptian Blue *only* became widespread by Fourth-Dynasty (*ca.* 2613–2494 BC). The Max-Planck Project identified Egyptian Blue as the blue pigment in all the Egyptian samples (more than 1300) they analyzed (from the Fifth-Dynasty onwards), apart from the grey-blue pigments of the First Intermediate Period (Blom-Böer, 1994). The blue of the dramatic head-dress and of parts of the neck covering of the Eighteenth-Dynasty Queen, Nefertiti, which can be seen in the Neues Museum in Berlin, has been identified as Egyptian Blue by Wiedemann & Bayer, (1982).

Sir Flinders Petrie's excavations at Tell el-Amarna at the beginning of the twentieth century, uncovered ancient stocks (sometimes called artists' pot specimens) of the raw ingredients used for the manufacture of Egyptian Blue. Also found, were sites (which he labelled as 'factories') for the production of the pigment Egyptian Blue; previously, in 1894, Petrie had uncovered bowl-shaped pans and cylindrical vessels or saggars that he suggested were used in antiquity to make Egyptian Blue. Provided that they are duly cared for and not subsequently contaminated, artists' pot specimens, such as found by Petrie, are important because their analysis should not produce fallacious chemical phases, but represent the product as left by the early artisan. However, they may, of course, have been subjected to weathering or chemical

degradation in the centuries that have passed since their production. These pot specimens may also yield information (relating to the manufacturing processes and the availability of ingredients) about the locality in which they were found.

More recent excavations at Tell el-Amarna by Barry Kemp (1989), found a very small number of these “fritting” pans. Kemp also uncovered various remaining, isolated, pieces of Egyptian Blue ‘cake’, which allowed the identification of five different categories of Egyptian Blue forms and the vessels associated with them: large round flat cakes, large rectangular flat cakes, bowl-shaped cakes, small sack-shaped pieces and spherical shapes.

At the ancient harbour town of Qantir (Pi-Ramesses), in Lower Egypt, founded by Seti I (1294 - 1279 BC) which later became the major seat of government under his son, Ramesses II (1279 - 1213 BC), fragments of small objects, in various stages of production were discovered early the twentieth century by Mahmud Hamza (1930). Also found were '*... lumps of the favourite blue colour (ie Egyptian Blue pigment) ...*' (Nicholson & Peltenburg, 2009, 184). Recent excavations at the same site by Rehren & Pusch (2005) were concerned with the early production of glass. Their evidence uncovered a substantial copper-based industry with evidence of bronze-casting, red-glass making and faience production, in addition to Egyptian Blue manufacture. Reaction vessels with adhering remains of Egyptian Blue were also found in the excavations (Shortland, 2012, 94) which suggests that the Egyptian Blue had been manufactured on site. The scarcity of finished Egyptian Blue products, at this site, however, may suggest the possibility that the locally manufactured Egyptian Blue cakes were exported to other areas where they would be worked into finished small objects or used to produce the pigment. Alternatively, of course, the lack of finished products at Qantir - Pi-Ramesses may simply reflect the presence of an efficient and well managed trading

organization whose stocks of finished artifacts were, perhaps, deliberately run down. In fact, there is no reason to suppose that such a well established local industry would not have had the facilities to produce Egyptian Blue, firing the cakes and regrinding the material if a pigment was to be produced. However, given the evidence, a more likely explanation is that a decision had been made to terminate the production of Egyptian Blue and to continue with the other, perhaps more profitable, well established industrial activities.

The finding of Egyptian Blue cakes at Zawiyet Umm El-Rakham, a Ramesside fort abandoned shortly after the reign of Ramesses II, near the Libyan coast (Hatton, Shortland & Tite, 2008, 1599) without evidence of any local manufacturing site, might be taken to suggest that the cakes had been traded and would probably be passed on to, or traded with, another location with a manufacturing capability. However, it is not clear why any manufacturing site would need to import cakes from elsewhere. Cakes that have been molded or pressed into the shape of small objects, or those waiting to be prepared for use as a pigment normally need to undergo at least a single further firing - hence the difficulty in explaining the presence of cakes in those (non-manufacturing) areas near the Libyan coast. It is possible that the cakes may have been used as 'currency', to encourage or facilitate trade with other areas by means of a barter economy.

The royal graves near the New Kingdom town of Karnak were serviced, by a nearby village of craftsmen who were responsible for their building and decoration. In 1999 Pagès-Camagna *et al.* analysed, using Raman microscopy and scanning electron microscopy, ... *seven cakes of raw Egyptian pigments* ... which had been excavated from the village. The colour of the cakes varied from different shades of blue to turquoise which, according to Pagès-Camagna are ... *associated with residues of the initial compounds and by-*

products...[of] ...the manufacturing process. The analysis showed the presence of calcium, silica, copper and, in some of the samples, tin.

2.3 The Occurrence and Use of Egyptian Blue outside Egypt.

As already noted, Egyptian Blue is first attested in Egypt during the Fourth-Dynasty, *ca.* 2613–2494 BC, although Hatton *et al.*, (2008) have suggested a considerably earlier date. There are no extant Egyptian texts describing its production. According to Spurrell (1895, 236) ... *Wherever Greek and Roman Colonies existed in the Mediterranean area it [Egyptian Blue] has been found extensively on buildings, sculptures, vases, ivory etc.* However there is no direct evidence to suggest that the technology was transferred from Egypt to other parts of the Mediterranean basin, or elsewhere in the Middle East; neither is there evidence to support the contention that parallel, possibly later, or an even an earlier, invention occurred outside Egypt. This suggestion does not exclude the possibility that modifications or adjustments to the technology invented elsewhere in the Mediterranean basin did not at some stage find their way back to influence the Egyptian production protocols. There were, for instance, significant trading connections between Crete and Egypt (Immerwahi, 1990): Minoan ceramics are found in many Egyptian cities and the Minoans imported several items from Egypt, most notably papyrus, and it is claimed that Egyptian hieroglyphs served as a model for the Minoan pictographs, which later developed into the Linear A writing systems (Bengtson, 2002); Linear B is thought have appeared later after the Minoans were over-run by the Mycenaeans. Furthermore, the strong indications of trade in glass ingots, and possibly finished items, during the Bronze Age (fourteenth century BC) between Egypt, Mesopotamia and several Mycenaean and Aegean cities (Jackson &

Nicholson, 2010) implies that the exchange of technologies between major centres was always a strong possibility.

In their 2007 paper, when considering possible international trade in Egyptian Blue pigments, Tite and Hatton tentatively suggest that there was some form of central control over the production of Egyptian Blue pigments. It may be suggested that this opinion is, for three reasons at least, unjustified. Firstly, it implies the existence, for which there is absolutely no evidence, of central areas of production, which could be regulated; secondly, it is based on the examination of 27 samples of Egyptian Blue from just six sites across the Roman Empire: Egyptian Blue pellets, in the form of balls, were examined from Memphis in Egypt, from Delos in the Aegean, from a shipwreck off the coast of Malta and from both Hertford and Colchester in England. The sample from Pompeii consisted of ground pigment contained in small pots; the Roman samples are from mosaic tesserae; and finally, because it fails to take into consideration the undoubted mobility of different ‘schools’ of painters who, during the course of their engagements, were likely to have acquired the Egyptian Blue pellets from many different sources. Hence, the location in which Egyptian Blue pellets might be found, may bear absolutely no relationship to the place in which the pellets had been manufactured.

From the third millennium BC, that is from the Early Dynastic III Period in Mesopotamia and elsewhere in the Middle East, Egyptian Blue is found as the material from which small artefacts and inlays have been created, though at this early stage there is no evidence of its use as a pigment, (Moorey, 1994). Riederer (1997) reports that Egyptian Blue has been identified at several Mesopotamian sites, including Persepolis, Pasargadae and Nineveh. From the seventh-century site at Nimrud, Tite *et al.*, (1984) have identified substantial blocks of Egyptian Blue that are thought to have been available for trade. In their 1987 paper Tite and colleagues examined a single sample

from each of Nineveh and Nimrud; the chemical analyses demonstrate that both samples have an otherwise similar chemical content, though the lime content in the Nineveh specimen is some 40% greater than that found in the sample from Nimrud. No explanation is offered for this difference, though elsewhere, Tite and colleagues (1984), suggest that Egyptian and Roman samples of Egyptian Blue have a higher calcium content than samples from Nimrud.

The dark blue material on a mace head from the Hurrian city of Nuzi (modern Yorghana Tepi, in northern Mesopotamia, south of Nineveh), dating to *ca.* 1500 BC has also been identified as Egyptian Blue (Moorey, 1994). Because of the early finds of Egyptian Blue in Mesopotamia, Moorey (1994) has suggested that it is possible that this material was first produced here, and not in Egypt. Egyptian Blue has also been found at the Roman fort, near the Azanathkona Temple, dating before AD 256, the date of its destruction by the Persians, at Dura-Europos, Mesopotamia, in modern day Syria.

An investigation of *in situ* wall-paintings and of powdered pigments isolated in ceramic vessels found at Herod's Palace in Jericho, dating to the first century BC, was undertaken by Silvia Rozenberg (1997). The powdered blue and green pigments were found to be identical to those used on the walls of the palace. The blue pigment was identified as Egyptian Blue. Rozenberg suggests that the high quality of the fresco work, the preparation of the walls according to standard Roman rules and the use of other imported colours strongly suggests that foreign, probably Roman, craftsmen were engaged at Jericho, and that these artists would have brought their pigments with them. This transport of coloured pigments by artisans is also suggested by Davey & Ling (1982).

Segal & Porat (1997) have reported finding wall-painting fragments from a 3rd -2nd century BC Hellenist fort at Acre. The colours were scraped off the wall-paintings by use of a scalpel and in two of the fragments Egyptian Blue was found, and in a third sample Egyptian Blue was found mixed with calcite.

During excavation of a Pompeian-style house, dated to the period 400 – 168 BC, in Pella, western Macedonia, samples of blue painted plaster were acquired for analysis and using non-destructive methods, [both XRD and XRF], by Calamiotou *et al.*, (1983) who were able to demonstrate that Egyptian Blue had been widely employed.

Several authors, including Segal & Porat, (1997), acknowledge that the pigment Egyptian Blue was widely adopted by different Greek civilizations. The Greek polymath Theophrastus, writing *ca.* 315 BC in his work *de Lapidibus* [On Stones, Chapter 98] mentions Egyptian Blue and the fact that it is synthetic. He states that there are natural and synthetic varieties of blue, *kyanos* (κύανος): the synthetic forms being Egyptian and Scythian Blue from Phoenicia – mentioning that both were made by combining sand, copper filings and flowers of soda, without describing the manufacturing process. He mentions Scythian or Phoenician Blue as another synthetic compound, different from Egyptian Blue. In fact, it seems that Egyptian Blue was traded by the Phoenicians and also possibly manufactured in the Levant, hence its ‘adopted’ name; and it is because of Alexandria’s significance as a trading port, that the pigment Egyptian Blue also came to be known as Alexandrian Blue.

From late Bronze Age sites in the vicinity of Thebes, 30 fragments of generally high quality wall-paintings, belonging to several contexts and periods, were investigated by Brysbaert (2008). Four of the blue samples were shown to be Egyptian Blue. Another blue sample was shown to contain

the blue sodic-amphibole, riebeckite, $\text{Na}_2(\text{FeMg})_3\text{Fe}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$ - the first time that this mineral has been identified on the Greek mainland.

Brysbaert and colleagues (2006) examined a total of 23 fragments of painted wall-plaster from sites in Crete, from Thebes and from Tell el-Dab'a in Egypt. Using laser-induced breakdown spectroscopy, Egyptian Blue was found in the blue samples from both Thebes and the Egyptian site. LIBS studies identified that the blue sample from Crete contained iron and magnesium: subsequent XRD studies concluded that the mineral was riebeckite.

Samples of painted wall-plaster were obtained for analysis from Knossos, Crete, made famous by Sir Arthur Evans' excavations at the beginning of the 20th Century. They were first examined by Noel Heaton (1910-11) who concluded that the paintings were ... *executed in true fresco technique* ... the pigments were mainly earth colours, the blue being Egyptian Blue. In 1976 Profi, with others, used non-destructive analytical techniques [such as X-ray fluorescence analysis (XRF), X-ray diffraction analysis (XRD) and mineralogical examination with a polarizing microscope] to ascertain what type of pigment had been applied to these frescos. Samples of the blue pigment from Knossos 4 and 5 were identified as Egyptian Blue whilst the sample from Knossos 6, dated to *ca.* 2100 BC, contained a sodium-magnesium-aluminium-hydroxide-silicate, the mineral glaucophane, $\text{Na}_2(\text{Mg}_3\text{Al}_2)(\text{Si}_8\text{O}_{22})(\text{OH})_2$, found locally in metamorphic rocks. Further work by Profi and colleagues continued on the Egyptian Blue samples and half of all the specimens examined contained this mineral. Tin was also found in the Egyptian Blue samples from Knossos, thereby implying that bronze products, as opposed to copper ores, were used in the manufacture of Egyptian Blue, at an earlier date than was the case in Thutmose III's Egypt, raising the possibility that this particular use may have been subsequently exported to Egypt. Filippakis *et al.* (1976), Jones (2005) and Hejl & Tippet

(2005) have shown the extent to which Egyptian Blue appears in Minoan frescos both in Crete, Phaistos, Kommos and Thera during the Bronze Age. Jones and Filippakis (1977) have demonstrated that a green pigment used on the island is produced by applying a yellow ochre mixed with or painted on top of either Egyptian Blue or a sodic-amphibole.

Using the same analytical techniques as those used on the Knossos samples, Profi and colleagues (1977) examined samples of blue pigment from the frescoes on the Greek island of Thera (Santorini) which had been excavated in 1866 shortly after a volcanic eruption. The famous French mineralogist, volcanologist, and administrator, Fouqué, was amongst those who participated in the excavation. More excavations took place in 1870 and 1967. As was the case at Knossos, a number of the Egyptian Blue samples found at Thera, and dating to *ca.* 1500 BC, demonstrated the presence of glaucophane. Also, on Thera, the related iron containing mineral, riebekite, $\text{Na}_2(\text{Fe.Mg})_3\text{Fe}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$, was isolated (Jones, 2005 & Profi *et al.*, 1977). Since both glaucophane and riebekite are found in local metamorphic rocks on Thera (and also at Knossos), the possibility exists that these blue sodic-amphiboles were mixed with the ingredients used to make Egyptian Blue during the manufacturing process, either deliberately, or more likely, as a result of soil contamination. Furthermore, analysis of sixteenth century BC samples taken from frescoes found at Thera showed that the identified Egyptian Blue also included tin products (Profi *et al.*, 1977).

In a recent study of the partially reconstructed wall-painting of the well known Archer Fragment in the Palace of Nestor, on the Greek Island of Mykonos, Brecolaki and colleagues (2008) have identified Egyptian Blue as the background colour to the area of the bow. This had been mixed with calcite to produce a light blue hue and had been applied above a grey undercoat.

On Cyprus, at Nea Paphos and Kourion, eight sites have been found in which Egyptian Blue (and no other blue pigment) has been found in Roman period wall-paintings. At none of these eight sites has any other element been found to suggested that anything other than ‘pure’ copper had been used in the production of the blue pigment (Kakoulli, 1996), *ie* there was no evidence of the use of bronze or any other copper-rich alloy: a finding that is not surprising given that Cyprus was known to be the principal source of copper during the Roman period. However, the author was not able to determine whether the Egyptian Blue found on Cyprus had been manufactured locally or had been imported.

During earlier excavations of the South East building in the forum at Corinth a collection of wall-painting fragments of mixed colours were found, together with a small ball (*ca.* 1 cm in diameter) of a blue pigment, and subsequently analyzed by Meggiolaro and colleagues (1997). All the blue pigmented fragments were associated with a calcite matrix which the authors suggest implies that the paintings were executed with a true fresco technique. The blue of the fragments has been identified as Egyptian Blue: in several of the blue fragments minute quantities of tin, magnesium, iron, and aluminum have been found. The small blue ball was also identified as being Egyptian Blue and it has been suggested that it represents an example of the raw material that was used in the production of the original wall-paintings, which subsequently were found as the fragments.

The use of Egyptian Blue in Etruscan wall paintings and in their frescoed tomb interiors is mentioned by Spurrell (1895, 236) and possibly pre-dates the use of the pigment in Rome itself. The Etruscans had close contacts with the inhabitants of the major Greek speaking areas to the south of their homeland in northern Italy and probably learnt of the use of Egyptian Blue from these contacts (Pontrandolfo, *et al.*, 2004).

There was extensive use of Egyptian Blue during the Roman period. Many local production centres and schools were established and a whole ‘army’ of painters became masters of its use both in Rome and elsewhere within Italy and throughout the Empire. Only in Roman texts is there an explicit description of the manufacture of Egyptian Blue found, such a description, if ever written, is not found in Egyptian works nor in those of any other ancient civilization. It is not certain at what date Egyptian Blue began to be produced in Roman Italy, though the first descriptions of its production process are found in the texts of Vitruvius (Book VII, Chapter XI, 1) writing in the first century BC. The pigment known as Egyptian Blue was described by Vitruvius by the term *caeruleum*^{*}, though he erroneously states that it was invented in Alexandria.

In one of the rooms of the baths of Emperor Titus’ palace in Rome, Davy (1815, 100) found... *several large lumps of a deep blue frit...* and in May 1814 he was present when ... *a small pot containing a pale blue colour* [-ed material] ... was recovered during an excavation in Pompeii and which was subsequently shown to contained ... *Alexandrian – [ie Egyptian] ... Blue.*

Fragments taken from wall-paintings in the Vesuvian area and bowls of powdered pigments found at Pompeii were investigated by Aliatis and colleagues (2010) using micro-Raman technology and other non-destructive techniques. Micro-stratification studies showed that in all the fragments of wall-paintings studied a beeswax layer was present. The authors suggested that this might have been a consequence of recent restoration work – the site

^{*} For most authors in antiquity *caeruleum* is used, like the Greek *kyanos*, to refer to the colour 'blue'.

was severely damaged by the AD 62 earthquake which preceded the destruction by eruption of Mt. Vesuvius in AD 79. Three blue samples, one fragment and two powders, were identified. One powdered sample was shown to be Egyptian Blue, but with it was found the lead mineral cerussite, PbCO_3 , which it was suggested might have been used to dilute the blue hue. The second blue powder was also Egyptian Blue and was associated with the high temperature polymorphs of quartz, *viz.* trydimite and cristobalite. The blue fragment from a wall-painting was also Egyptian Blue, but also demonstrated calcite, gypsum and beeswax. A violet coloured powder also contained Egyptian Blue which had been mixed with haematite grains, Fe_2O_3 . Egyptian Blue was found in two other wall-painting fragments: the analysis demonstrated that the first was mixed with other compounds, *viz.* haematite, cinnabar, HgS , minium, Pb_3O_4 , and goethite, $\text{FeO}(\text{OH})$. A second, green coloured fragment, was also shown to contain Egyptian Blue, but was mainly composed malachite, $\text{Cu}_2\text{CO}_3(\text{OH})_2$, and also contained smaller amounts of haematite, goethite, quartz, calcite, cerussite, albite, $\text{NaAlSi}_3\text{O}_8$, and massicot, PbO . The finding of so many powders with mixed pigments possibly suggests that they had recently been prepared and were shortly to be employed – before nature so cruelly intervened.

Piovesan and her colleagues (2011) have investigated some 57 fragments of wall-paintings and floor filling material from the Temple of Venus at Pompeii. On seven of the samples, all of which date from the Augustan and Julio-Claudian periods of construction, Egyptian Blue was found to have been used. In the two pale blue samples, a phase containing tin was identified as small inclusions within the cuprorivaite, $\text{CaCuSi}_4\text{O}_{10}$ crystals, implying that the copper had been sourced from a bronze material. The remaining five fragments, from a possibly different period, in which Egyptian Blue had been used showed no evidence of tin inclusions and were, therefore, manufactured

using a copper ore or metal; the implication being that two different methods of production of Egyptian Blue had been used. In each of these five samples, the Egyptian Blue had been mixed with, or covered with, other coloured pigments, including green earth.

The *Domus Aurea*, built by Nero in AD 64, was obliterated some 40 years later and its remains lay beneath newer constructions. Today it remains beneath the ruins of the Baths of Trajan. Being the largest palace in imperial Rome it was sumptuously decorated and is said to have had a magnificent Gilded Vault. Using MOLAB and a range of other technologies Clementi and colleagues (2011) investigated the pigments used in the decoration of the Gilded Vault. Egyptian Blue was identified on a number of samples. It was also identified at sites where the blue colour had turned black and elsewhere in combination with other pigments. Egyptian Blue was also identified in all the analysed green areas; in some areas the Egyptian Blue had been mixed with green earths; Egyptian Blue was also found in some of the purple areas where it seems that it was mixed with, or painted over with a red lake. In some areas micro-stratigraphy demonstrated five successive paint layers. The authors note that their results showed that pigments were seldom used alone but very often as complex blends.

During an excavation of the House of Diana at Cosa, Grosseto, Italy (dating to *ca.* 71 BC) forty samples of painted plaster were selected for an in depth study by Damiani *et al.*, (2003, 343). Chemical and mineralogical analytical techniques were employed in order to try and establish ... *the provenance and the technological utilization of the raw materials used for the pigments ... for the reconstruction of ancient trading patterns ... The identification and quantification of the pigments within the House of Diana gave further information regarding cost-accounting ...* Analysis of one of the painted samples showed that the pigment Egyptian Blue had been used and the

identification of a small amount of tin in the sample indicated that material from a bronze product or from scrap metal had been used instead of a copper ore. However, in another blue painted sample from the same site a copper ore, possibly malachite, had been used, no tin being identified. The production of Egyptian Blue, using two different copper sources, from the same period, on one site, had not been previously recorded.

Mazzocchin (2003) and colleagues used a range of analytical methods [optical microscopy, SEM-EDS, X-ray powder diffraction (XRD) and Fourier transform infrared spectroscopy, FT-IR] to investigate 60 fragments of wall paintings found during archaeological excavations at a Roman Villa in Vicenza, in north-east Italy. There were 5 pigments with a blue hue. All five were found to have been painted using Egyptian Blue, two were, however, diluted with calcite, calcium carbonate, CaCO_3 .

Throughout the late Roman period and into the early Middle Ages the use of Egyptian Blue as a pigment declined and the manner of its production was thought to have been forgotten. Indeed, it had been assumed that the technique for manufacturing Egyptian Blue had been lost by the late Roman period. Spurrell (1895) for example states that ... *there is no trace of it in any mediæval paintings* ... and Laurie (1914/1967) was of the opinion that the latest date for samples from Italy were the second to seventh centuries AD.

However, recent work has proved that these opinions were groundless: Riederer summarizes 'late' appearances of the pigment in Christian wall paintings in his 1997 paper. The pigments used on a ninth century Byzantine fresco, an *Assumption*, possibly dated to AD 850, in the Church of San Clemente, Rome, were compared with 'standard samples' of Egyptian Blue obtained from the first century AD fresco *Domus Augustana* in Rome, and from an excavated site at Aquilia. The results showed that Egyptian Blue had

been used as a pigment on this ninth century painting. The poor quality of the pigment used might suggest that the painters had access to an old source of the pigment from within Rome itself (Lazzarini (1982). However, it is now believed that Egyptian Blue was still being manufactured in the former Roman provinces of Asia Minor and Greece where traditional technology had not been forgotten (Lazzarini, 1982) and this might have provided an alternative source from which the artist obtained his material.

In 2000, Pozza *et al.*, published their study on the Photoluminescence of Egyptian Blue, Han blue and Han purple. The analytical non-destructive techniques that were employed were photoluminescence spectroscopy and x-ray diffraction (XRD). The aim of their research was to examine pigments identified in fresco and tempera wall-paintings. Small samples of pigment were obtained from the *Last Judgement*, a painting by the 12th century artist Nicolaus Johannes. The painting is presently held by the Vatican Museums. The unequivocal finding of Egyptian Blue, used as a large area of sky in the background of the picture, can only mean that the material was still being used into the Middle Ages; it does not, of course, necessarily mean that Egyptian Blue was still being manufactured in Europe at that time.

Egyptian Blue has also been found at sites in Switzerland (Béarat, 1996; Fuchs & Béarat, 1997 and Bugini & Folli, 1997) and France (Spurrell, 1895, and Ullrich, 1979) and elsewhere throughout the Empire. The most northerly finds have been made in Norway where Rosenqvist (1959) reported Egyptian Blue on a third century AD painted shield; however, it would be right to be somewhat sceptical of this claim since it was made without the advantage of modern investigative technologies, at a time when it was thought that Egyptian Blue could be identified following examination with a hand lens. The same hesitation about making premature diagnoses was expressed by Ann Brysbaert (and colleagues, 2006, 1098) when she writes that the initial

microscopic examination of a sample from Crete which was initially thought to be Egyptian Blue was *a clear proof that plain optical microscopic examination with a stereomicroscope is not sufficient to determine the composition of these materials.*

In 1999 Smith and Barbet examined, using Raman Microscopy, a blue pigment found in a garland of flowers on a painting from a Roman tomb near the necropolis at Kertch, in what is now the Ukraine. The results showed that Egyptian Blue had been applied to the wall painting. Smith and Barbet compared the results with a sample of an Egyptian Blue pellet taken from an artist's collection discovered near the Azanathkona Temple at Dura-Europos. The results were the same as those found in the Roman tomb.

During the Han Dynasty in China (208 BC to AD 220) a barium-copper-silicate compound, commonly known as Chinese, or more correctly, as Han Blue was used as a pigment, as Egyptian Blue was, further to the west. This material produced a deep lilac to purple colour. There is no evidence to suggest that the Chinese version had Egyptian roots, or indeed that the Egyptian pigment had an eastern origin. Han Blue is an analogue of the calcium-copper-silicate used in West. Nevertheless, it has been suggested, without any evidence to support the notion, that Egyptian Blue could have travelled along the so-called Silk Route and reached China, where local materials were adopted in the manufacturing process (Chiari & Scott, 2004). Since the production of Han Blue involves the same sort of manufacturing process as does Egyptian Blue, it will also inevitably result in the production of phases other than the main pigment, such as wollastonite, quartz and glass, Kendrick and colleagues (2007) have shown that the alkali-earth analogues wesselsite, $\text{SrCuSi}_4\text{O}_{10}$, and effenbergerite, Han Blue, $\text{BaCuSi}_4\text{O}_{10}$, may be synthesized, though the colours of these synthetic products lack the intensity of synthetic calcium-copper-tetrasilicate, Egyptian Blue. In this 2007 paper

Kendrick *et al.*, investigated the structural and colour properties of the Egyptian Blue family of pigments, and have demonstrated that prolonged exposure to natural light has a deleterious effect on the colours of all of these synthetic products, leading to the darkening seen in historic samples, something of which most archaeologists and art historians have been aware for decades, if not longer !

2.4 Egyptian Blue pigment found at Romano-British sites.

Egyptian Blue has been found as artefacts or as a pigment at a number of Romano-British sites including Woodeaton (Jope & Huse, 1940), Wroxeter (Bushe-Fox, 1915), Silchester (Spurrell, 1895) and Darenth (Spurrell, 1895). Spurrell (1895) records that in these last two sites the Egyptian Blue is ... *of the pale cheap kind*.

On receiving samples of painted plaster from the renowned antiquary Samuel Lysons (who with the aid of John Hawkins and many others excavated Bignor Roman Villa from 1811 to 1819, following the discovery of a large mosaic by George Tupper whilst ploughing his field), Sir Humphry Davy wrote a short letter to him (dated 14th June 1815) confirming that ... *The blue is a frit, or artificial ultramarine, composed of peroxide of copper, silica, and alkali* ... and goes on to say that it ... *is of the same kind as the colour said by Vitruvius ... which was manufactured in his time at Pueoli*. Having previously completed his research and written his paper Observations upon the Composition of the Colours found on the Walls of the Roman House discovered at Bignor in Sussex Davy spoke about his findings to the Royal Society on 15th June 1815, only some four months after giving a reading of his investigations into the pigments found at Pompeii and ancient Rome.

In the 1970s Egyptian Blue was found on a Romano-British site at Shakenoak Farm, north of Oxford, and was examined by Atkins (1970) using X-ray powder diffraction. The results showed that it was Egyptian Blue... *a calcium-copper silicate ... [5%] ... of the material from the interior nodules consists of various impurities including quartz, calcite and limonite*. Atkins also compared the Shakenoak samples with pure synthetic Egyptian Blue data obtained from Pabst's studies (1959); the comparison suggested that the Shakenoak blue pigment was ... *very pure*. The Shakenoak material had not been ground and may have been used as a ... *stock material intended as a paint pigment* and it was unlikely that it had been manufactured on site but was imported, (Atkins, 1970).

A W G Lowther carried out an extensive excavation at Ashted Roman Villa, Leatherhead, Surrey, during 1927, 1928 and 1930 and found amongst the artefacts were three pellets of Egyptian Blue. According to Gower ... *The Ashted pellets are not particularly noteworthy, being very typical of examples of Egyptian Blue pellets found in Britain* These were subjected to visual examination by the author, Gower, and by Justine Bayley, from the Ancient Monuments Laboratory; no scientific analysis took place. It was concluded that these samples represented stock which was intended to be used as a pigment for internal decoration of the villa, (Gower, 1984).

Egyptian Blue was found in sediments on two different archaeological sites in west-central England and, according to the authors, (Canti & Heathcote, 2002), this is the first time that Egyptian Blue has been identified from micro-stratigraphic samples. The first find occurred in centrifuged heavy mineral separates from Roman layers beneath a car park in the Roman town of Cirencester. The sediments formed part of a suite of road surfaces and included the fill of a ditch, all dating to before the 3rd century. Individual grains of less than 500 µm were hand picked and selected for analysis. The

second sample was found in soil destined for micromorphological studies, in Mill Street, Wantage, Oxfordshire, in Saxon sediments. Three grains were found in two thin sections produced for soil micromorphological studies; no loose material was available. Analyses were therefore restricted to techniques suitable to a thin section. Analytical techniques used for the study were optical analysis, scanning electron microscopy, energy dispersive X-ray analysis and X-ray diffraction. The results of the investigations showed that the samples were the pigment Egyptian Blue. The authors were unable to provide an explanation for the presence of their finds since, for instance, the nearest copper ore deposits and copper working sites were at a considerable distance from the two locations. It is assumed that the finds were discarded, or lost, by artisans using the pigment in the area. The authors also undertook experimental work using a modified recipe obtained from Chase's paper; the resulting Egyptian Blue pellets were fired, re-ground and fired again in order to obtain a successful result.

A study undertaken by Clegg and Freeman on twenty-seven Egyptian Blue pellets found during the 1997, 1998 and 1999 excavations at Fishbourne Roman Palace, Chichester in West Sussex, was published in *Sussex Archaeological Collections*, 141, (2003). All the pellets were analyzed using XRF, the results of which showed differing quantities of calcium, copper and silica. Lead and tin were also detected in some of the pellets. This study suggested that there was no standard recipe used for the manufacture of the Egyptian Blue pellets found at Fishbourne Roman Palace.

2.5 The Method of Production of Egyptian Blue. In his text *De Architectura*, (Book VII, Ch XI) Vitruvius details the manufacture of Egyptian Blue, described as a common (or austere) pigment, discussing how it

was produced by grinding sand, copper and natron and by heating the mixture, shaped into small balls, in a furnace. He fails to mention lime, a major component of Egyptian blue though, it is probable that lime-rich sand was used; desert sand can contain up to 18% lime (Tite & Shortland, 2003). Vitruvius (Book VII, XI, 1) also records that a factory to produce Egyptian Blue had been established, by Vestorius in Puteoli (modern Pozzuoli) in Campania, and that the material produced was also known, at least locally, as Puteolanum or Pozzuoli Blue and also as Vestorianum or Vestorian Blue. In his text Pliny (Book XXXIII, 57) also mentions the use of natural blue materials which he describes as being mined in Cyprus, Scythia and Egypt, but adds that of all the blues, Egyptian [Blue] was the best.

One of the earliest known studies of synthetic blue pellets occurs in a paper entitled *Some Experiments and Observations on the Colours used in Paintings by the Ancients*, by Sir Humphry Davy, LLD, FRS, which was read to the Royal Society on 23rd February 1815, and subsequently published in the Philosophical Transactions of the Royal Society, 105, (1815). In this paper Davy thanks his good friend Canova, who had responsibility for the care of ancient art works in Rome, for allowing him to collect samples of different pigments, found in vases, in the ruins of Emperor Titus' palace in Rome. Davy acknowledges the slightly earlier work of the French chemist J A Chaptal (1809), who investigated colours found in a colour shop in Pompeii. Two of the colours were blues ... *which he considered as compounds of alumina [Al₂O₃] and lime [chaux, CaO] with oxide of copper [d'oxide de cuivre, CuO]*. In one of the rooms in the baths of the palace, Davy found... *several large lumps of a deep blue frit ... which when submitted to various chemical analyses were found to contain minute quantities of lime and ... sulphate of soda, which proves that it was a frit made by the means of soda, and coloured with oxide of copper* In May 1814 Davy was present

when ... *a small pot containing a pale blue colour* [-ed material] ... was recovered during an excavation in Pompeii and which was subsequently proved to contained ... *Alexandrian frit* - ie Egyptian Blue. Apart from these observations, Davy appears to have been the first to manufacture this material in modern times and when describing *Alexandrian frit* he says ...[it] *may be easily and cheaply made; I find that fifteen parts by weight of carbonate of soda, twenty parts of powdered opaque flints, and three parts of copper filings strongly heated together for two hours, gave a substance of exactly the same tint, and of nearly the same degree of fusibility, and which, when powdered, produced a deep sky blue...*

After a gap of nearly eighty years other papers began to be published on similar looking blue pigmented material. A specimen of material obtained from Roman ruins at Autun in central France was analysed by Fontenay (1874, 193-199) who described it as *bleu égyptien*. He also undertook experiments (using 25 parts CaCO_3 , 15 parts CuO , 70 parts white sand and 6 parts of Na_2CO_3) that after firing led to the successful production of the pigment and recommended that a sodium flux no greater than 7 wt % should be used. Dr W J Russell's paper of 1892, published as Chapter VIII (*Egyptian Colours*), in W M Flinders Petrie's book *Medûm* examined blue pellets found in the Egyptian towns of Gurob (Eighteenth-Nineteenth-Dynasty) and Kahun (Twelfth-Dynasty). Although blue-green, green and purple pellets were found at these sites (and later manufactured by Russell), he states that the blue pellets ... *are by far the most interesting ones ... their existence may serve to indicate to some extent the manufacturing skill and knowledge of the producers. They vary greatly in tint...* After thoroughly examining these pellets Russell wanted to know ... *how exactly they were made, what furnace would be necessary...* He went on to undertake experiments to emulate these ancient craftsmen. Of the materials used, Russell was of the opinion that

silica ... *was the principal constituent, and formed perhaps 60 to 80% of the whole mixture; then there was the copper to give the colour, no doubt merely the crude mineral, but almost any salt of copper would produce the same effect.* For Russell, that ... *copper was the colouring-matter in these frits there could be but little doubt...* His experiments showed that it was important to maintain a high temperature as well as maintaining ... *the length of time of heating ...* He goes on to state that the ... *colour of the frit depends principally ... upon the amount of copper it contains ...* and says of the ingredients that ... *the blue pigments ... contain comparatively small amounts of copper, perhaps 3 to 10 %...* and that lime and sand were used with ... *10 % of potassium and sodium carbonates.* These ingredients were fused together in order to produce what would now be referred to as Egyptian Blue. Russell was well aware of the important effect that the sand could have on the final product ... *at all events it is certain that a very small amount of iron [combined with the silica] modifies the colour to a very considerable extent.*

In 1889 the French geologist Ferdinand Fouqué gave a detailed description of the texture of the very pellets that had been shown to Davy at Pompeii in 1814. He was the first to identify the material, now known as Egyptian Blue, as the calcium-copper-tetrasilicate, cuprorivaite, $\text{CaCuS}_4\text{iO}_{10}$, (Laurie *et al.*, 1914; Kendrick *et al.*, 2007) and identified its crystalline structure to be of the tetragonal system, and its specific gravity to be of the order of 3.04. Fouqué also defined the optical characteristics of the crystals which he described as being ... *scales flattened parallel to the base of the prism, and often jagged at the edges, sometimes, however, ending in clear rectangular outlines They are of a beautiful azure blue* (quoted in Laurie, *et al.*, 1914, 419). Another important finding by Fouqué was that Egyptian Blue could be produced without the aid of a soda or potash flux, a finding which was later confirmed by Laurie (1914).

In 1895 F C J Spurrell published, in volume 52 of The Archaeological Journal, a paper entitled *Notes on Egyptian Colours* detailing his in-depth study of the blue pellets found at a ‘factory site’ during excavations at Tell el-Amarna by Flinders Petrie. He described in great detail his understanding of the manufacturing process and the ingredients of the pellets which consisted of fine sand which was ... *difficult to procure free from iron ... copper ore was always malachite and the alkali was either native potash or soda and included the use of limestone* He continues by saying that ... *the bowls of frit, sometimes flat bottomed, sometimes rounded, rested [on structures] so that the furnace could be raked under them ...* After the firing and cooling of the pellets ... *the best parts were selected, ground and re-heated in shallow pans ... [which] ... intensified the frit, making it uniform ...* in an attempt to improve the hardness and uniformity of the material. He notes that from the Fourth Dynasty the object was to produce a ... *brilliant blue of moderate depth*. However, in later periods various shades of blue were produced, ... *some by intention in manufacture, or some by admixture. After the Nineteenth Dynasty true blues were made but mostly a lower tone was affected ... being sometimes little better than grey, or the powder of roofing slate ...* as determined by the fashion of the time. Both green and lilac coloured material was found amongst the debris found at Petrie’s ‘factory’ sites. Green material is commonly produced and reported by most authors who have attempted to manufacture these pellets (see Bianchetti, *et al.*, 2000; Russell, 1892 and Spurrell, 1895). Additionally, Russell (1892) states that lilac material can be produced by adding ... *a large proportion of lime ... and a great increase in the copper* to the recipe.

Dr A P Laurie, together with Messrs McLintock and Miles, published a paper in 1914 entitled *Egyptian Blue* in The Proceedings of the Royal Academy, volume 89. In order to successfully re-produce Egyptian Blue in their own

laboratory Laurie and his colleagues conducted a large series of experiments. They describe the method of producing Egyptian Blue pellets, the firing times and the type of furnace that they suggest was used by the Egyptians, from information gained following a reading of Spurrell's 1895 paper. Laurie and his colleagues obtained samples of Egyptian Blue pellets which they carefully examined following Fouqué's description of its texture and comments about its crystalline structure. It is said that Fouqué's descriptions (of 1889) are somewhat ambiguous, if not misleading, due to his commercial interests with a French manufacturer of Egyptian Blue material (Warner, 2007, 41). Laurie's team undertook further studies on additional samples from various sources extending over different periods of time, such as ... *the lid of a coffin of the XIth Dynasty and a piece of Roman fresco on the Palatine Hill, a piece of the crude frit from the Manchester Museum, a piece of crude frit occurring among Dr Russell's samples, two samples from Viriconium, [Wroxeter Roman Villa] in Shropshire, a sample obtained in Syria, ... and some of Dr Russell's 1892 samples ... from Gurob...* and found that all the samples had the same crystalline structure, as indicated by Fouqué's analyses.

Laurie and colleagues followed Russell's method of repeated grinding, heating and firing of the ingredients. They used a mixture of calcium and copper oxides, silica and a flux. The recipe they used was adapted from that of Russell and consisted of silica 64.6g, copper carbonate 15.4g, calcium carbonate 12.4g, with 7.2g of sodium carbonate (Na_2CO_3 , natrite) as the flux: the ratios of these components being: 4.2 : 1 : 0.8 (and 0.5 for the flux).

Laurie and colleagues also extended the firing times from 16 to 48 hours and they increased the temperature of the muffle furnace from 760°C to 900°C, (though on one occasion the temperature rose to 1150°C). As a consequence of their series of experiments it was concluded that to successfully produce Egyptian Blue crystals the temperature should remain at 850°C and the firing

time last for 48 hours. Temperatures below this critical range resulted in the production of unfused materials; higher temperatures resulted in the production of a greenish glass. They also found that if too much flux was added to mixture, the manufacturing process resulted in the formation of glass; on the other hand no flux at all was needed if the long firing time at 850°C was preceded by firing at much higher temperatures. They concluded that the flux (usually sodium or potassium salts) did not enter into the final crystal formation, but merely acted to bring the three ingredients (copper, calcium and silica) into combination at the optimum temperature of 850°C. Indeed, they suggested that the presence of a molten glass phase provided the medium in which the components could chemically react within the melt and thus exsolve the various crystalline phases, thus distinguishing the process from a solid-state sintering process. This work by Laurie and his colleagues was the first modern attempt, in which the scientific method is fully described, to synthesize the pigment known as Egyptian Blue.

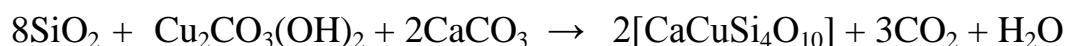
In 1971, after he became interested in studying Egyptian Blue *artefacts* found in the department of Ancient Near East Art at the Metropolitan Museum in New York, W T Chase (1980) began a series of experiments to produce Egyptian Blue objects. In all he conducted a series of six experiments using different combinations of ingredients, each experiment being subject to different firing times. He noted Laurie's formula or recipe and adopted his own, his Formula II (the most successful) was identical to that used by Laurie and his colleagues, except that the 7.2g of sodium carbonate, natrite, was replaced with 7.2g of so-called synthetic natron consisting of 3.2g sodium sesquicarbonate, 2.1g of sodium sulphate and 1.5g of sodium chloride (*NB Chase's listed amounts do not add up to 7.2g*). The temperature used in his Formula II, was 830 °C and with a firing time greatly reduced to 45 minutes he produced ... *a nice blue* ... which corresponded to the blue found on one of

the studied artefacts – a ‘sistrum handle’. In the oxidizing atmosphere used, Chase found that the cuprorivaite phase disappeared if the temperature was raised to 1000 °C and held at that level for a duration of one hour. However, he stated that the cuprorivaite crystals could be regenerated if the resulting glassy mixture were fired again at 850 °C for a prolonged period. This particular feature had also been noted by Laurie.

It is to be noted that Chase is, in fact, describing the production of a coarse, ‘pre-fired’, sintered material that would in ancient times have then been moulded into any one of a number of small objects, which would normally have needed to be re-fired before acquiring any commercial potential. He makes no claim to have produced a pigment.

Following these and more recent studies, *eg* by Ullrich (1985) and Tite *et al.*, (1984 & 1987), it is established, unequivocally, that Egyptian Blue is produced by heating together, in an oxidizing atmosphere, a mixture of silica, copper and calcium, normally together with an alkaline flux. According to Blom-Böer (1994) the three principal ingredients used in the early period, *viz.* the Fourth-Dynasty (*ca.* 2600 BC) of the manufacture of Egyptian Blue in Egypt were: silica in the form of quartz sand, the copper ore, malachite, $\text{Cu}_2\text{CO}_3(\text{OH})_2$, and calcite, CaCO_3 , with potash or natron (sodium sesquicarbonate, $\text{Na}_2\text{CO}_3\text{NaCHO}_3 \cdot 2\text{H}_2\text{O}$,) as a flux, all of which components were found naturally within Egypt itself. Malachite, for instance, is found in both the eastern desert regions and in the Sinai peninsula; there are also indications of ancient workings at the Wadi Arabah near the present-day Israeli boarder. Some of the other ancient mining sites, such as that at Wadi Maghara were associated with much smaller amounts of other copper containing minerals, such as azurite (chessylite), $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$, and chrysocolla, $(\text{CuAl})_2\text{H}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$. There is, however, no conclusive evidence to suggest that malachite was ever used as the *main* copper

ingredient in the manufacture of Egyptian Blue in Egypt. The ingredients are ground, mixed together, and moistened with a little water and rolled in the hand, being shaped into small balls, which are heated at a high temperature, which Blom-Böer said was lowered to *ca.* 743°C, by the presence of the flux. According to Riederer, (1997) the mixture should be heated to 900 – 1000°C with the temperature maintained at 800°C for a period of 10 to 100 hours. Temperatures below these levels, he claims, are likely to produce un-fused materials or glass and slags. The heating process turns the silica, malachite and calcite to cuprorivaite, carbon dioxide and water as shown in the following balanced equation:



The major product of this reaction is the calcium-copper-tetrasilicate cuprorivaite, $\text{CaCuSi}_4\text{O}_{10}$, (written as $\text{CaO} \cdot \text{CuO} \cdot 4\text{SiO}_2$ by Fouqué). To obtain the idealized end product of only the blue crystals of cuprorivaite with no unreacted quartz or the formation of glass or other unwanted phases, the *theoretical* percentages of the ingredients used – when no flux is employed – should be approximately (according to Tite, *et al.*, 1987) silica 64%, copper oxide 21% and calcium oxide 15%, *ie* the ingredients should be mixed in a ratio of: 3 : 1 : 0.7. However, these authors acknowledge that all ancient samples examined contain, in addition to Egyptian Blue, various amounts of unwanted components, including a glass phase.

The natural mineral cuprorivaite was first isolated on material recovered from Mount Vesuvius by Carlo Minguzzi, who published his findings in 1938. However, it is found naturally in concentrations too small to provide a viable pigment source. Pabst, working in Berkeley, California, was the first to suggest, in 1959, that cuprorivaite was the natural analogue of the pigment known as Egyptian Blue. The synthetic form has been found as crystal

fragments from a copper smelting furnace in Arizona (Mazzi & Pabst, 1962); similar findings have been reported by Ivanov (1938) and colleagues.

In recent ground breaking *laboratory* experiments Pradell, with Tite and others (2006) have investigated the development of cuprorivaite crystals, and other phases during the manufacturing process, both during the heating and during the subsequent cooling of the mixed ingredients. Much of the following description is based on the material of that paper. All of the ingredients, the quartz powder, the artificial malachite (copper carbonate hydroxide 1-hydrate) and the calcium carbonate, had a grain size of less than 53 μm ; the mixture was divided into two lots which were then mixed with a 3 wt % and with a 0.3 wt % portion of soda (Na_2O) flux respectively. Both portions were mixed and pre-fired to 700°C to drive off water of hydration. These two lots of cooled, pre-fired, dark grey, sintered material were then reground to pass through a 500 μm sieve and (in the first experiment) one portion was used for each of the low and high alkali mixtures.

Subsequent XRD analysis demonstrated, in each lot, the presence of quartz, SiO_2 , tenorite, CuO , calcite, CaCO_3 , and a disordered phase that was thought to be trona, $\text{Na}_3\text{H}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$. In the high alkali portion only, sodium carbonate, natrite, Na_2CO_3 , was also found.

For the second experiment a further two portions (with a high and a low soda flux respectively) of the cooled, pre-fired, dark grey, sintered, reground and sieved material were used for high-temperature XRD analyses. This mixture was heated to 675°C before the furnace temperature was then increased at a rate of 5°C/min. until it reached 1000°C, (*ie* for 65 minutes). The material was then cooled to room temperature at a constant rate of 10°C/minute. During the heating and cooling stages high-temperature XRD measurements

were made with the assistance of a high photon flux provided at the European Synchrotron Radiation Facility at Grenoble. From the XRD data the percentages of the different crystal phases that were formed were calculated. In the experiment with a high alkali mixture, the following information was obtained as the temperature increased:

- In the temperature range of 700 – 800°C there is decomposition of sodium carbonate and the formation of soda;
- At a temperature of *ca.* 850°C calcite starts to decompose to form lime, CaO, and Ca₂CuO₃;
- Above 850°C a sodium silicate is formed;
- Between about 850 and 950°C the amounts of quartz and tenorite progressively decrease;
- At 950°C lime reacts to produce wollastonite, CaSiO₃;
- Between 950 and 1000°C the sodium silicate disappears and a corresponding decrease in the total crystalline phases suggests the formation of a melt, from which cuprorivaite crystallizes;
- Finally, at *ca* 1000°C some of the quartz converts to cristobalite.

During the cooling phase cuprorivaite crystals continue to form until the temperature reaches *ca.* 700°C. During this stage there is also an increase in the formation of wollastonite and quartz and a slight decrease in cristobalite. Analysis shows that the percentages of the final cooled mineral composition are: cuprorivaite 40 wt %, quartz 37 wt %, wollastonite 17 wt %, tenorite 3 wt % and cristobalite 3 wt %.

The high temperature XRD analysis for the mixture with a low alkali flux level shows similar patterns, though with some notable differences, *viz.* neither wollastonite nor cuprorivaite appear until the temperature reaches 1000°C. During the cooling stage cuprorivaite stops forming at the higher temperature of 850°C, suggesting that the crystals nucleate but do not grow very much during the subsequent cooling, in contrast to the high alkali mix.

Analysis shows that the percentages of the final cooled mineral composition are: cuprorivaite 26 wt %, quartz 41 wt %, wollastonite 16 wt %, tenorite 13 wt % and cristobalite 4 wt %.

In a third series of experiments, bulk samples of the high and low alkali prefired and reground, sieved, dark grey material, that had *not* proceeded to high-temperature analysis, were formed into small compacted discs which were fired (for a second time) at 1000°C for a period of 1 hour. The bulk composition of the Egyptian Blue pellets were examined in cross-section using a SEM which indicated that ... *the high-alkali mixture consisted of abundant elongated Egyptian Blue crystals, up to 50µm in length, intermixed with occasional quartz particles (that have been partially converted to cristobalite), and all bonded together by an extensive glass phase to form a uniform microstructure across the sample.* In contrast, high magnification of the SEM analysis of the low alkali specimen demonstrated elongated Egyptian Blue crystals (up to 30µm in length) that are in some cases partially separated by very small areas of glass. Occasional scatterings of small unreacted copper oxide particles are visible. The glass phase is much less extensive than in the high-alkali mixture ... *so that the microstructure is less uniform across the sample and consists of isolated clusters of Egyptian Blue crystals adhering to partially reacted quartz particles.* The authors suggest that in the high alkali mixture a greater glass phase develops and it is the formation of a melt from which the cuprorivaite crystals continue to grow, even during the cooling phase, that produces the characteristic SEM picture.

The paper concludes with a consideration of the impact that the study might have for the understanding of the manufacturing process of ancient specimens of Egyptian Blue. The authors are clear that a glass phase is only to be found in samples from Egypt; in contrast, in samples from the Near East, the Aegean and Europe the glass phase is absent, presumably because of

weathering. But in all the ancient specimens that have been analyzed the abundance and morphology of Egyptian Blue crystals and the uniformity of their microstructure matches those of the high alkali replicate mixtures, and never those of the low alkali replicate mixture. Thus, in all the ancient specimens examined, the Egyptian Blue crystals were formed (it is claimed) through nucleation and growth within a liquid or glass phase from mixture that would have included, as a minimum, a few percent of an alkali flux.

In the real (non-laboratory) world in which Egyptian Blue was manufactured for commercial or artistic purposes in antiquity the process undoubtedly became well established and highly regulated over the course of time. Manufacturing processes that were in some way “irregular”, with activity outside specified limits, could have disastrous results. As a simple example, it is suggested that if for any reason the firing temperature exceeded 1050°C then the resulting pellets would be found to be unstable (Jaksch *et al.*, 1983). Again, unauthorized or ill-advised manufacturing activity could result in the production of excessive amounts of unwanted mineral components, *ie* phases other than cuprorivaite, such as wollastonite, CaSiO_3 , or tenorite, CuO , that might prove detrimental to the intended use or colour of the pigment finally formed.

The type, amount and ratio of ingredients employed in the manufacturing process have a significant effect on the texture, composition and other features of the manufactured pigment pellets. Samples taken from ancient specimens of Egyptian Blue show, when subjected to analysis, considerable variation in their bulk composition.

If, as would seem to have occurred frequently, desert sand, which is invariably associated with iron, is used as the source of silica then, when finally produced, the Egyptian Blue pigment would include small amounts pyrite,

FeS₂, and titanomagnetite, Fe₃O₄Fe₂TiO₄. Jaksch *et al.* (1983) found crystals of this last mineral in samples collected from the tomb of Sabni, in Aswan, of the Sixth-Dynasty, confirming that desert sand had been used in the manufacturing process at that time. Similarly, the Max-Planck project, (Blom-Böer, 1994) demonstrated that in all the samples of Egyptian Blue analysed, both pyrite and titanomagnetite were found. This study, involved the analysis of 1,380 pigment samples, (most of which were of Egyptian Blue obtained from paintings on stone surfaces and wall paintings from the Fifth-Dynasty to the early Roman period, but with a majority of samples obtained from Thebes) extended over a twelve year period. Similarly, Scott (2002) observed the presence of pyrite in several Fifth-Dynasty tomb paintings, even though pyrite, FeS₂, is said to decompose at temperatures greater than 743°C – suggesting, possibly, that the ingredients were far from thoroughly mixed and, possibly, poorly ground, so that in the furnace there existed, as it were, protected ‘microclimates’ where the temperature was lower; this phenomenon is not unknown in manually ‘controlled’ firing processes. The use of desert sand from Egypt, which can contain significant amounts of other elements (for instance 2 - 18% lime, up to 2% iron and 1 - 4 % alumina) should be compared with the (virtually) iron-free crushed quartz pebbles that were used in the New Kingdom site at Qantir and at Tell el-Amarna, which according to Tite & Shortland (2003) contains 99.83% SiO₂ with minute amounts of lime, soda and alumina, Al₂O₃.

By the time of the reign of Thutmose III, (1479 – 1425 BC), *ie* during the early New Kingdom period, copper ore, possibly malachite, Cu₂CO₃(OH)₂, was replaced in Egypt, in some cases at least, by filings from copper ingots or from bronze scrap as has been deduced by the presence of the tin oxide, cassiterite, SnO₂, in the end product (Jaksch *et al.*, 1983). No copper ores have been found in Egypt that contain significant amounts of tin oxides; the

reasonable assumption is, therefore, that the tin oxide found in the manufactured pigments was a result of replacing the copper ores, possibly malachite, by fragments or filings from copper products and possibly also scrap metal fragments, when very small amounts of arsenic and lead might also be found.

Because the manufacturing process was not mechanized but depended on individual (usually, skilled) human input, and because of limited local availability of some ingredients, all of the historic Egyptian Blue pigments that have been analyzed have been found to contain phases in addition to the desired cuprorivaite. Thus, if during the manufacturing process an inattentive operative adds more calcium, in the form of excess lime, CaO , calcium carbonate, CaCO_3 , or even gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, to the ingredient mix than copper, then the mineral copper wollastonite, $(\text{CuCa})_3\text{Si}_3\text{O}_9$, forms and the resulting pigment shows a distinctive green hue (Jaksch, *et al.* 1983). Additionally, very small amounts of copper wollastonite also appears as minute crystals within the interstices of the cuprorivaite. According to Tite (1987) if more calcium than copper is added during the preparatory phase then ... *Egyptian Blue crystals are not observed. Instead the excess CaO is precipitated from the glass, typically, as calcium silicate, ie wollastonite ($\text{CaO} \cdot \text{SiO}_2$) and the CuO remains dissolved in the glass to produce the characteristic pale blue colour...*

Similarly, if excessive amounts of a copper ingredient is incorporated into the mixture then copper oxides such as cuprite, Cu_2O , and tenorite, CuO , may be found (Tite *et al.*, 1984) and variable amounts of unreacted quartz and a glass phase are also likely to be present as unwanted phases. The appearance of iron products following the use of quartz sand has been mentioned.

On occasions, less common minerals are found in examined Egyptian Blue specimens. Thus in material from Knossos, dated to *ca.* 2100 BC and from Thera (Santorini) dated to 1500 BC, glaucophane, $\text{Na}_2\text{Mg}_3\text{Al}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$, and the related iron containing mineral, riebeckite, [discussed above] have been isolated.

It is perhaps not surprising that the bulk composition of samples of Egyptian Blue pigments show a geographical variation. Thus Tite, *et al.* (1984) have shown that Egyptian and Roman specimens tend to have excess calcium oxide, CaO, lime, and higher concentrations of alkali when compared with samples from, for instance, the great Assyrian city of Nimrud. Specimens from the latter have an excess of copper oxides and lower concentrations of alkali, whether derived from plant ash or natron, *ie* lower levels of both sodium and potassium. At these sites, as at virtually every other site, there is more silica than is required for stoichiometry.

During analysis of the blue pigment samples found at the Eighteenth-Dynasty 'factory site' at Tell el-Amarna, Weatherhead and Buckley (1989) drew attention to the *present* obvious visual difference between the turquoise blue pellets and the blues of other pellets. Turquoise, and lapis lazuli, were much admired semi-precious stones that, it is thought, many Egyptians coveted, hence, it is suggested, that attempts appear to have been made to imitate these stones. The authors have also suggested that the turquoise hue could be mimicked in Egyptian Blue production if significantly higher amounts of sodium, in the form of impure natron, were included as part of the manufacturing process.

But it is not only the nature, the amounts and the ratios of the ingredients used that affect the end product: the manufacturing process itself is a major factor in determining the texture, structure and colour of the resulting pigment. The

extent to which the ingredients are mixed together, the size of the powdered granules, the number of times the fired pellets are reground, the number of times the mixture is fired, the duration of the firing times, the firing temperatures, the rate at which the furnace temperature is increased and the rate of cooling, and the amount and nature of the alkali flux, if used, all contribute to determining the hardness, the texture and the colour of the manufactured pigment.

There appears to be an intimate relationship between texture and the colour of the manufactured pigment (Tite *et al.*, 1984 & 1987). When the ingredients are prepared in what might be called the ‘standard fashion’ and fired once according to the established recipe, the resulting pigment has a visibly coarse texture. At the microscopic level the structure shows large irregular clusters or aggregates of coarse crystals of cuprorivaite which adhere to the unreacted quartz. Such a product is usually found in the form of small blocks, cakes or slabs (in the early Dynastic periods) and as small balls (in later Dynastic periods and until the Greco-Roman Period) and it is suggested that these could have either been waiting to be processed through a second stage, where they would be ground, or they would have been used as a blue pigment or possibly molded to the shape of variety of low value small artifacts, before being re-fired to produce the desired object (Tite *et al.*, 1984).

Because of its microscopic structure, of clusters of crystals, this coarse form of cuprorivaite is relatively thick and produces a characteristic dark blue colour. According to Tite *et al.* (1987) this dark blue, coarsely crystalline Egyptian Blue, shows significantly high levels of the alkali flux. However, large aggregates of crystals could be achieved without the alkali flux, but longer firing times at higher temperatures were required. Such a requirement was also found by Canti and Heathcote (2001) in their small scale study to produce Egyptian Blue. Although the authors managed, by multiple cycles of

grinding and firing at 1000°C to produce an Egyptian Blue pigment with large amounts of dark unreacted crystal aggregates, the greater proportion of their output consisted merely of a grey-blue sintered powder.

To produce a fine-textured Egyptian Blue pigment a second manufacturing stage is required. The coarse cuprorivaite crystals are subjected to a second grinding to produce a fine powder that is mixed with water and the paste reformulated, before re-sintering, for a second time, at a temperature range of 850 – 950°C for one hour (Tite *et al.*, 1984 & 1987) or longer. In general, the finer the powder produced by grinding, the smaller the particles that are sintered and the paler the resulting pigment (Ullrich, 1985). The result is a finely texture cuprorivaite pellet whose crystals, at the microscopic level, are seen to be uniformly interspersed between, and intimately linked to, the unreacted quartz grains. This product will be of a light blue hue. Tite *et al.*, (1987) demonstrated that such a product also has a relatively low alkali content. It is said that an alkali content of below 1% does not allow glass to form and the resulting Egyptian Blue would be softer, with a hardness of 1 – 2 on the Mohs scale (Tite *et al.*, 1984).

In the same paper Tite *et al.* go on to show that an even paler shade of blue pigment, assigned the name diluted or pale light blue, is produced if manufactured in a similar fashion to the light blue material, but with higher amounts of an alkali flux used in its production cycle. Because of this (relatively) high alkali content the resulting material has a significantly greater proportion of unreacted quartz embedded in a glass matrix and is therefore much harder, though remaining finely textured. The ‘paleness’ of the blue colour is due, it is suggested, to the extensive glass phase which ‘masks’ the blueness of the material. These harder, finely textured, relatively glass-rich forms of Egyptian Blue are often found in the Eighteenth-Dynasty and later

and their production is thought to have been influenced by advances in glass technology (Lee & Quirke, 2009).

Flux was considered to be an essential ingredient in the process of manufacturing Egyptian Blue pigments by Weidemann and Bayer in their 1982 study. The presence of a flux was considered necessary if the deepest blues were to be produced since the flux was understood to catalyse the production of the larger crystals (sizes of 5–50 μm) upon which the colour intensity depended. (Jaksch, *et al.* 1983).

According to Tite *et al.*, (1987) in all the samples of ancient Egyptian Blue specimens that have been analyzed the alkali content is greater than 1%, suggesting that the flux was deliberately added to the other ingredients and not merely the result of the use of impure components. However, the amount of alkali used in the production of Egyptian Blue seldom exceeds 4% and this may make its identification in ancient samples difficult, particularly because of the possibility of leaching. (This low percentage can be compared with the Egyptian glass manufacturing process, for instance, where the alkali flux is of the order of 10 – 20% of the total component weight). In the Late Bronze Age glass manufacturing process, plant ash was the normal alkali (Rehren & Pusch, 2005) which can be identified by its potash, phosphorus, magnesia, lime and sometimes iron content. It is likely that use of plant ash as the flux was also continued during the manufacture of Egyptian Blue. Sodium sesquicarbonate, natron, $\text{Na}_2\text{CO}_3\text{NaCHO}_3 \cdot 2\text{H}_2\text{O}$, is a natural evaporitic deposit containing few impurities, and is also a common source of the alkali flux, and has been found at the Wadi Natroun and at El-Kab; Tite and his colleagues (1984) suggest that natron was the alkali most commonly used in the production of Egyptian Blue. On the other hand, analysis by Jaksch *et al.* (1983) of various samples of Egyptian Blue, identified variable amounts of

phosphorus (up to 2% by weight), suggesting that the alkali source used was plant ash and not natron in the samples they examined.

Although it is technically possible, as discussed above, to produce Egyptian Blue pigments without the use of a specific flux, *a priori* this is highly unlikely to have happened in antiquity for the simple reason that the ingredients used were seldom, if ever, free from contamination of one sort or another.

This review demonstrates that the major effort of research into the study of the Egyptian Blue pigment is concerned with its production and manufacture, in Egypt, within Mediterranean Basin and elsewhere. For this reason significant reference is made to the controversies surrounding the materials used as the ingredient mix and to the method of production. The literature also includes a large amount of material relating to the laboratory manufacture of Egyptian Blue material. There is, however, a relative shortage of material relating to the use of Egyptian Blue, used as a pigment, on wall- paintings, particularly at Romano-British sites.

Egyptian faience and Egyptian Blue production are both very old industries. Faience objects have a distinct core and separate glass layers which makes them relatively easy to distinguish from objects made from Egyptian Blue. However, glass objects may sometimes be difficult to distinguish from those made with Egyptian Blue: this is especially true in the New Kingdom as Egyptian Blue at that time became more refined and glassy in structure. The influence of glass production (which really only begun during the reign of Thutmose III, 1479 – 1425 BC) appears to have had a significant influence on the manufacturing process of Egyptian Blue in the later periods. Furthermore, the expanding copper industry associated with Thutmose III resulted in copper filings or other copper products, rather than the copper ore malachite, being

employed in the Egyptian Blue recipe, as indicated by the presence of tin oxides in the Egyptian Blue pigment, as mentioned above.

It is generally thought that the use of Egyptian Blue became less common as the Roman Empire retreated. Humphrey Davy (1815), for instance, attributes the loss of the skills involved in its production in areas of the former empire to be due to the description given by Vitruvius whose recipe fails to mention explicitly that a calcium component is a prerequisite. However, the damage done to the remaining Empire by invading barbarians surely played a not insignificant rôle in the decline of artistic achievements and the production of artistic materials.

2.6 Other Blue Pigments used in Antiquity

(a) **Azurite**. According to Lucas, (1934) the natural mineral azurite was commonly used as a pigment for wall paintings in antiquity in Egypt. In Book XXXV, 28 Pliny mentions the expensive rich blue mineral azurite, also known as chessylite, $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$, known as *armenium* in antiquity and commonly found with malachite. Armenian azurite was said to cost 300 sesterces per pound whereas an inferior version found in the provinces of Spain was much less expensive. Azurite is a naturally occurring, blue carbonate of copper found in Sinai and the eastern desert regions of Egypt. Spurrell in 1895 noted its use in a Fourth-Dynasty context near Rahotep where it is found in a shell used as a palette ... *which has the remains of a beautiful blue smeared over its interior*. He also states that pure azurite is found ... *on the mouth and eyebrows painted on the fine cloth which covers the face ...* of the Fifth-Dynasty Ranefer mummy which is now to be found at the Royal College of Surgeons Museum, in London, and on a number of Eighteenth-Dynasty wall-paintings (at a time when the use of Egyptian Blue was well established).

However, no examples of azurite were found by the Max-Planck Project; Ingrid Blom-Böer (1994) suggests that the apparent absence of azurite from the Egyptian palette was perhaps a result of its poor quality and its impermanence as a pigment, though the above mentioned findings of Spurrell seem to contradict such a suggestion. When ground finely, its colour becomes a pale blue (Pastoureau, 2001). According to Gettens & Stout (1966), azurite was coarsely ground in order to achieve a dark blue colour; it was easy to recognise by its sandy texture and it would have been applied to a tempera medium (Gettens & Stout, 1966).

(b) Malachite. Many earlier authors suggest that malachite, $\text{Cu}_2\text{CO}_3(\text{OH})_2$, was the copper pigment most commonly used in the manufacture of Egyptian Blue, as mentioned above. It is also suggested that it was the most commonly used green pigment. Thus in describing the colours found at Kahun (XII Dynasty) Spurrell (1895, 227) states that ... *the greens are copper silicates ... (chrysocolla) ...* $[(\text{CuAl})_2\text{H}_2\text{Si}_2\text{O}_5(\text{OH})_4.n\text{H}_2\text{O}]$... *or malachite ...* and when describing the colours used at Medûm (IV Dynasty) he states that the greens are pure malachite; likewise when describing the colours from Tell el-Amarna (XVIII Dynasty) he states that the copper ore was always malachite, crude and roasted. He does, however, acknowledge that malachite was scarce and that it was often used as a thin surface layer supported by a yellow marl.

(c) Indigo. Pliny talks of indigo, (*indicum purpurissum*), *indigofera tinctoria*, $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2$, being used by the [Roman] painters as dividing lines ... *that is for separating shadows from light ...* (Book XXXIII, 57, where it is also called Indian blue). Indigo, according to Eastaugh and colleagues (2004) was used as a pigment in the first century AD in Roman paintings, and was ... *most valued ...* as one of the organic blue pigments. There appears to be no suggestion that indigo was ever used in Egypt or elsewhere in the Middle East or Mediterranean area in antiquity.

(d) **Lapis Lazuli**. Writing in 1955 Forbes records that the known blue pigments of antiquity, generically known as *caeruleum* or *kyanos*, were restricted to lapis lazuli, azurite, indigo and Egyptian Blue. Also known at the time were turquoise and cobalt.

In 1815 Davy examined blue pigment samples found in one of the areas in the baths of Titus. As they contained various amounts of carbonate of lime he used an acid (which he called nitro-muriatic (or marine) acid, a combination of nitric and hydrochloric acids) to dissolve the lime and the result showed a ... *very fine blue powder similar to the best ... ultramarine* ... Calcite, as found for instance, in the rock known as lapis lazuli, is dissolved by dilute hydrochloric acid. It is therefore possible, though perhaps unlikely, that Davy had found that lapis lazuli had been used as a pigment – the residual fine blue powder would, therefore, have been grains of lazurite. Lucas & Harris (1962) report that the lapis lazuli pigment, ultramarine, was not attested [in wall-paintings] before the eleventh century AD and Lucas (1934) suggests that ... *there is no proof that this* [ground lapis lazuli, ultramarine] *was known until about the beginning of the eleventh century AD*. According to Forbes (1955) there appears to be absolutely no record of lapis lazuli, or of turquoise, being ground and used as a pigment before the sixth or seventh centuries AD, indeed it was thought unlikely that these semi-precious stones, much sought after in antiquity, would ever, at that time, have been subjected to such degradation. In contrast to such statements Theophrastus, writing in the fourth century BC, is reported to have said that lapis lazuli, ... *a stone common among us in the tops of snuff-boxes ... of which the glorious blue colour called ultramarine by the painters, is made*. (De Lapidibus, 83). Forbes (1955) notes that the expensive mineral lapis lazuli (but not its ground form) was known in the Ancient Near East: it was a major component in the famous so-called Standard of Ur, found in the Royal Sumerian cemetery at Ur and dating to *ca.* 2600 BC; it is first mentioned (in any

text) in the Sumerian epic story of Gilgamesh, dating to about 2750 BC: the poet Sîn-lēqi-unninni tells us ... [to] *Find ... the copper box marked with his name ... take out the tablet of lapis lazuli. Read how Gilgamesh suffered ... and accomplished all ...* (Mitchell, 2004, 9).

Forbes (1955) also noted that ... *a cake of lapis lazuli* ... was reported to have been found, as a pigment, in Sargon's palace at Khorsabad, the Assyrian capital city that was abandoned following Sargon of Akkad's death in 705 BC and Spurrell (1895, 236) states that Egyptian Blue was an ... *early subject of barter between Egypt and the East, together with its superior, lapis lazuli.*

Notwithstanding the opinions of Forbes (1955) or of Lucas and Harris (1962), the lapis lazuli pigment, ultramarine, was used in the Roman period, if not earlier in the East. Thus, in their study of fragments taken from the wall-paintings in the Vesuvian area and of bowls of powdered pigments found at Pompeii, Aliatis and colleagues (2010) found some blue spots on one wall-painting fragment that were conclusively demonstrated to be lazurite, the major component of lapis lazuli. Furthermore, Brysbaert (2006) has identified lapis lazuli (lazurite) used as a pigment in a mixture with a purple hue found on a 13th century BC Greek Bronze Age wall painting from Gla, a fortified site in Boeotia, mainland Greece. Brysbaert suggests that the ancient artisans had the knowledge to produce and use this pigment on wall plaster paintings.

Pagès-Camagna and Colinart (2003) consider Egyptian Blue to be a lapis-lazuli substitute, just as they claim that Egyptian Green was a substitute for the natural pigment, turquoise. Ground lapis lazuli (ultramarine) can produce a wide range of differing blues: its preparation requires considerable skill over a period of time and due to its high cost, it is mainly used in small areas of a painting. When used by the Roman artists preparation was usually haphazard as they did not separate out the blue crystals (from the calcite, pyrite and other possible

minerals), hence the blues that had been applied to the lime mortar were less rich than those seen in paintings found in the Ancient Near East (Pastoureau, 2001).

It is worth noting that in paintings on vellum and other portable materials, indigo or woad is notoriously difficult to distinguish from lapis lazuli. Several major studies of the blues found in the illuminated pages of the Lindisfarne Gospels and the Book of Kells (both eighth century AD), and earlier manuscripts, for instance, were definitively described as lapis lazuli until the blue areas in question were conclusively identified as woad or indigo by use of micro-Raman studies (Meehan, 2012).

(e) **Cobalt Blue** Spurrell (1895) stated that cobalt had never been found on wall-paintings but acknowledged that it had been used in the making of blue glass in the eighteenth dynasty and later, in Egypt and in Mesopotamia. However, cobalt is now attested in Egypt from the Tell el-Amarna period and is found on pottery, but again not on wall-paintings. A source of the cobalt has been reported from the western desert oases of Kharga and Dakhla, (Kaczmarczyk, 1986 and Shortland *et al.*, 2007) though a central European provenance has also been thought to be a possibility - there appears to have been intensive Aegean-Egyptian trade contacts – either directly or via Syria – during the reigns of Amenhotep III and Akhenaten in the late Eighteenth-Dynasty which might have provided the network for a cobalt supply from the far side of the Balkans. Geologically, cobalt is not found as a native metal but normally as a by-product of nickel and copper exploration or mining. In the form of salts of aluminium, CoAl_2O_4 , cobalt has been used historically, particularly in Chinese blue and white porcelain from the time of the Tang Dynasty, AD 618-907 (Enghag, 2004); it has also been attested in Egyptian sculpture (but not on wall or other paintings) and in Persian jewellery from the late bronze age. Its use in Egyptian glass, glasses and faience dates from the

time of the Eighteenth-Dynasty, *ca.* 1550 -1292 BC, (Rehren, 2003 and Lucas, 1934).

2.7 Egyptian Green

Green, and purple pigments, and pellets, were found with the debris as well as blue pigments in early studies (*eg* by Russell, 1892); all of the Egyptian Blue pigments that have been analyzed have been found to have excesses of some components or unwanted phases. As already discussed, if during the manufacturing process excess lime (CaO), calcium carbonate, CaCO_3 , or even gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, is added to the ingredient mix then the mineral copper wollastonite, $(\text{CaCu})_3\text{Si}_3\text{O}_9$, forms and the resulting pigment shows a distinctly green hue (Jaksch, *et al.* 1983). Mazzocchin and colleagues (2004) have shown that cuprorivaite decomposes at temperatures greater than 1050°C and in the presence of sodium carbonate results in the formation of a green frit,

The pigment known as Egyptian Green has, often, a turquoise hue and was known to have been used in antiquity in foliage decorations; for long it has been considered to be a pale version of Egyptian Blue (*eg* by Weatherhead & Buckley, 1989), or as a misfired Egyptian Blue (*eg* Bayer & Wiedemann, 1976; Jaksch, *et al.*, 1983 and Ullrich, 1985) or even as a weathered Egyptian Blue. Pagès-Camagna and Colinart without explanation, state in their 2003 study that Egyptian Green was a substitute for the natural pigment turquoise; they go on to demonstrate that Egyptian Green is a pigment distinct from Egyptian Blue.

Although Egyptian Green and Egyptian Blue have an almost identical chemical composition the latter authors claim that as a result of the manufacturing process two distinct pigments can be produced. They appear conclusively to be able to distinguish, on the basis of the CIE L^*a^*b colour analysis (which system

is, of course, less subjective than the Munsell charts), between visually different coloured cakes of historic material and thereby demonstrate that there are indeed two different coloured pigments. An SEM study of the cakes also appeared to distinguish between the two pigments: the Egyptian Blue scan showed cuprorivaite crystals, $\text{CaCuSi}_4\text{O}_{10}$, in a silica rich amorphous phase, whereas the Egyptian Green scan shows wollastonite crystals, CaSiO_3 , in a copper rich siliceous amorphous phase. Studies were also undertaken on 50 archaeological fragments taken from paintings kept in the Louvre museum, though no details are provided about the sampling conditions, sample sizes, substrate material or provenance, for example. The authors continued with experimental studies looking at the mineral content of a fired mixture, consisting of silica sand, copper oxide and calcium carbonate with a sodium carbonate flux between 7 and 12 [wt] %, as the furnace temperature increased and subsequently decreased. It is not recorded how the mineral content was recorded at each temperature stage but the results presented are significantly different to those recorded by, Pradell, with Tite and others (2006), discussed above. For instance, Pagès-Camagna and Colinart (2003) do not record that both cuprorivaite and wollastonite appear during the cooling phase, as well as during the heating stages, although they state that the cooling rate is a significant factor in determining colour, and that wollastonite is the main marker for Egyptian Green. They conclude that the following conditions are found when Egyptian Green is created:

- the firing temperatures are higher than those for Egyptian Blue *ie* higher than the 870-950°C at which Egyptian Blue is formed;
- there is less copper than calcium in the original mixture;
- the bulk Ca/Cu ratio is greater than 1.7, and the bulk SiO_2/CuO ratio is greater than 4 [in Egyptian Blue the ratios are said to be of the order of 0.7 and 3 respectively];

- there is a significant level of a soda rich flux, typically between 5.7 and 10 wt % whereas in Egyptian Blue it is always five or less;
- There is a significant copper concentration, CuO, in the silica rich amorphous phase, shown on the SEM;
- the characteristic presence of (copper)-wollastonite in the pigment.

Thus they conclude that Egyptian Green, a copper containing wollastonite-type compound, is formed by varying both the proportion of the materials selected and the production conditions used to produce Egyptian Blue. The nature of the bulk Ca/Cu and SiO₂/Cu ratios mentioned as being necessary for the production of Egyptian Green mirror the observation by Jaksch *et al.*, (1983) that an excess of lime or other calcium compounds added to the ingredient mixture will result in the final pigment having a green hue. Overall, therefore, it is possible to conclude that there is almost certainly a mineralogical distinction between the two pigments but, it is suggested, the case presented by Pagès-Camagna and Colinart (2003) is somewhat confused and lacks clarity, perhaps because they are writing in a language which is not their mother tongue.

Many of the findings of Pagès-Camagna and Colinart (2003) appear at first sight to be corroborated by Bianchetti and colleagues (2000) who, in a series of experiments that consider the manufacture of Egyptian Blue, suggest that wollastonite was detected in mixtures containing a lower copper to calcium ratio. They also noted that when the firing temperature is raised to 1015 °C cuprorivaite is transformed into green glass (a green frit) and that wollastonite was always detected in green frit. However, their overall conclusion is that ... *the presence of wollastonite and green frit cannot be strictly connected, so that wollastonite cannot be regarded as a certain indicator of the presence of green frit ... and that ... it was possible to obtain – from the same constitutive materials of Egyptian blue – an artificial green colour, a green frit, by a moderate raising of temperature or by using fluxes; this reconstruction may be*

compatible with the ancient Egyptian technology of glass production. Many of the earlier investigators of Egyptian Blue production, including Spurrell, would, it may be suggested, agree with this finding.

Indeed, Spurrell (1895, 234) found specimens from Tell el-Amarna and Gurob that were both blue and green carbonates of copper. He suggested that when a mass of the fired pigment was broken up and examined it was ... *commonly found that part was green and part blue, mottled and shaded in a beautiful manner.* Subsequently the best (*ie* blue) parts were selected, reground and re-fired to produce blue cakes. Spurrell (op.cit.) was of the opinion that a green pigment was ... *sometimes a step in the process of making the blue... But green could also be made by employing sand highly stained with iron; the careless use of which ruined many a batch intended for blue* (Spurrell, idem.). However, he suggested that such greens were rarely used since they were inferior to malachite and he acknowledged that it was difficult to find sand free of iron.

It has been suggested that pigments described as being of a green hue or even as being an Egyptian Green pigment may be the product of weathering and degradation of the multiphase Egyptian Blue pigment. Schiegl and colleagues (1992) have shown that some superficial green surfaces on painted stone surfaces of Old and Middle Kingdom samples were originally Egyptian Blue. They showed that the glass phase of Egyptian Blue can devitrify, resulting in the secondary formation of copper compounds such as copper chloride and malachite and a corresponding green hue to the pigment.

CHAPTER 3

Methodology

By different methods different men excel

Charles Churchill, 1731-1764, priest and poet

3.1 Preamble

In order to facilitate the understanding of past civilizations, archaeologists – and to a lesser extent historians - have, particularly since the 1960s, begun to interact with specialists within fields such as analytical chemistry, physics, statistics, geology and environmental sciences. Pollard and Heron (1996) have suggested that these and other specialities can provide the archaeologist with numerous approaches and techniques which ... *facilitate data analysis and interpretation, enhancing the opportunity to extract more information from the material record of past human activity*. In the light of such an understanding, Archaeological Science may be viewed, according to Tite (1991), as a group of various sub-specialities in which the main activities include:

- eg the study of the provenance, use and technology associated with discovered artefacts (Glascock *et al.*, 2005);
- eg the investigation of environmental issues such as climate change, animal husbandry, land management, and consideration of the diet, health and welfare of those who lived on a particular site (Chepstow-Lusty *et al.*, 2007);
- eg the use of non-destructive techniques, such as geophysics and aerial photography, for the location of buried features (Clark, 1990);

- eg the use of chemical and physical dating methods that provide the archaeologist with absolute and relative chronologies (Bowman *et al.*, 1991); and
- eg the conservation of artefacts: involving the study of the decaying process and the development of new methods for reconstructing and preserving these objects (Watkinson, 1987 and Barham & Goodman, 2005).

These various scientific approaches frequently have the potential to supply precise and detailed information upon which improved archaeological interpretations can be based. Furthermore, as Greene (1995) suggests, using tried and tested scientific methods can only enhance the design and conduct of archaeological research. Aitken, (1990) in his studies, goes yet further and suggests that *... scientific dating is not just a boring necessity that tidies things up by providing numbers, it is vital for valid interpretation.*

3.2 Analytical techniques used in sample preparation

In the present study it was necessary to establish the chemical and mineralogical composition, texture, fabric, structure and geochemical classification of each of the sampled Egyptian Blue pellets and of the blue and green fragments of painted wall plaster. It was therefore vital to determine what types of quantitative and semi-quantitative geochemical analyses would be most suitable for this purpose. This is particularly important given the requirement that all the samples examined in this study, being of archaeological value, were required to be analysed using non-destructive (or absolutely minimally destructive) techniques. Initially all the Egyptian Blue pellets were weighed and measured. The pellets, together with fragments of painted-plaster, had their colour identified using the Munsell Book of Color (Matt Finish Collection) 2001, (see appendix A). Samples were also examined under a MEIJI techno RZ zoom Stereomicroscope with a fibre-optic light source to permit study in fine detail

their textural composition, structure and fabric. The data presented using these methods are, therefore, purely qualitative and the results are intended to show the general characteristics of each pellet and fragment of painted plaster. The method used to prepare the samples taken for investigation are described along with the analytical technique employed in their analysis.

Laser Ablation Inductively Coupled Plasma-Mass Spectroscopy (LA-ICP-MS) is a multi-element analytical technique that is able to produce detection levels in the range of a few parts per million, and is therefore used when elements are present in very small quantities. It requires a small sample size for the analysis and is therefore technically micro-destructive, though the damage is normally so small as to be invisible to the naked eye. The method has been used as an important analytical tool in earth sciences since the 1990s and according to Sylvester (2001), ... *it can be argued that earth scientists have been the major driving force behind the development of ...* LA-ICP-MS. The technique is also used in environmental sciences and has been applied to analyse fish scales, bone, teeth, mollusc shells and tree rings (Veinott, 2001). The technique can be applied to solid samples, such as Egyptian Blue pellets, without preparation. In the context of this study it was observed that there was a developing link between the investigative techniques being employed in geological research and their applicability to archaeological studies. Disadvantages involved with the LA-ICP-MS technique include the high purchase cost, the lack of calibration standards and the need to use a nebulizer and spray chamber for liquid samples.

During initial studies for this project it was noticed, during the literature search, that recent papers had been published on the successful use of LA-ICP-MS in archaeological sample characterization. The use in archaeological research of this investigative technique has been extensive in the United States for several years, especially in establishing trade patterns, for example, concerning the manufacture of obsidian artefacts (the origin of obsidian artefacts can be traced

chemically since each volcanic source has a distinctive “fingerprint”) from the Aztec-Tarascan frontier and also at El Ujuxite in Guatemala, Speakman *et al.*, (2005). It is evident that LA-ICP-MS has an established pedigree in archaeological research, particularly in the USA, though presently less so in the United Kingdom. It is one of the techniques of choice in the present study. The data presented for this study from LA-ICP-MS are qualitative and the results are intended to show the general elemental composition of each pellet and fragment of painted plaster. The reliability of the data obtained from the LA-ICP-MS is paramount: the manufacturers of the New Wave Research Merchantek UP-213 Laser Ablation System, which was used to analyse the Egyptian Blue pellets, have produced a software programme that meets the analytical needs of this research project.

The Egyptian Blue pellets from several Romano-British sites were characterised using an Agilent 7500ce ICP-MS equipped with a New Wave Research Merchantek UP-213 Laser Ablation System, operated in scanning mode. Operational parameters were as follows: Argon gas was used throughout at a flow rate of 1.25 litres/min; laser ablation spot size was 10µm, with a pulse frequency of 10Hz, a scan speed of 10 µm/sec and an energy density of 3J/cm². Before analysing the pellets a gas blank was run to ensure that the ... *carrier gas* 's [Argon] *flow into the* [LA-ICP-MS ablation chamber was] *a high velocity jet directed on to the ablation site...* (Jackson, 2001). Each of the pellets were placed separately, without any preparation, inside the chamber where ablation of the sample took place. During ablation the laser beam obliterates a very small section of the sample which produces a cloud of very small particles which are removed by the carrier gas (Argon) and are passed into the ICP plasma for analysis the results of which are shown within seconds on a computer screen. LA-ICP-MS has a distinct advantage over other geochemical analytical methods, including its ability to determine the concentrations of a wide range of elements,

minimal sample damage, a rapid turn-over, low cost and typically good precision and accuracy. In addition, when undertaking LA-ICP-MS studies there is little risk of the sample becoming contaminated because it remains intact within its original matrix throughout the procedure.

Perhaps the most frequently used method of investigation described in published archaeological research papers is **Scanning Electron Microscopy with Energy Dispersive X-ray Micro-analysis (SEM-EDAX)**. In this investigative technique an image can be magnified from x 20 to more than x 80,000 – very many times more than would be possible when seen under an ordinary optical microscope. Unlike an optical image, the SEM uses an electron beam to produce high resolution images with a large focal depth and is, therefore, able to produce images that provide a good representation of the three-dimensional structure of the sample since a large amount of the sample can be in focus at one time. A further great advantage of the SEM-EDAX as an analytical tool is that the researcher can see clear and detailed images of the sample on a computer screen, from samples no larger than 10µm in diameter. Using X-rays to analyse the relative energies emitted by the back-scattered electrons it is possible to accurately determine what elements are present in each sample. Disadvantages of the SEM-EDAX include its high cost and rather bulky mass, its inability to produce colour images and its sensitivity to vibration and external magnetic and voltage fields; its location must therefore be carefully chosen. According to Kuisma-Kursula (1999) SEM-EDAX is known to have a poor sensitivity to trace elements and to all elements lighter than sodium (RAM, 22.99). This opinion supported Reed's statement (1996) in which he states that the theoretical detection limits for SEM-EDAX are about 0.08 % (*ie* 800 ppm) by weight. Trace element concentrations in archaeological specimens are commonly below this level. Furthermore, the sample must be stable under vacuum and must be electrically conductive (Killick, 1996); however,

conductive coatings such as gold (Au) and palladium (Pd) can overcome many of the latter two problems. In the present study both gold and palladium were applied to samples from the Egyptian Blue pellets using a sputter coater.

A Scanning Electron Microscope (SEM) equipped with an Oxford Instrument Analytical ISIS system and an Energy Dispersive X-ray Spectrometer (EDAX) was used to analyse all of the samples used in this study. In the application of SEM-EDAX, minute samples (weighing < 0.1g) were taken from each of the Egyptian Blue pellet and mounted on 12mm aluminium pin stubs, using sticky carbon tabs (Agar Scientific) to hold the particles in place, each with its own ID. In order to increase the electrical stability and reduce the possibility of charging effects, it was necessary to coat the samples with palladium (Pd) using a Polaron SC7640 sputter coater. Once dried the samples were loaded into the chamber of a JEOL JSM 6310 Analytical Scanning Electron Microscope.

X-ray Powder Diffraction (XRD) is a method of investigation, based on the early work of Bragg, and formulated as Bragg's Law, that provides both a quantitative and a qualitative analysis of the compounds being studied. The method involves beaming an X-ray at the subject material and then measuring the diffraction of the beam from different parts of the sample. By analysing the resulting diffraction pattern the unique atomic structure of the sample can be recorded. It thus allows identification of different crystalline phases (and the degree of crystallinity), the presence of amorphous phases and the size and orientation of crystallites. According to Skoog and Leary (1992) XRD ... *provides a convenient and practical means for the qualitative identification of crystalline compounds ... an X-ray diffraction pattern is unique for each crystalline structure.* However, the method is less accurate when analysing smaller samples so that materials that are present in only trace amounts will often go undetected thereby possibly producing skewed results. Another disadvantage is the high purchase cost of the equipment.

X-ray Powder Diffraction was used to verify the mineralogy of two fragments of painted plaster from St Albans which were analysed using a PANalytical X'Pert Pro X-ray diffractometer to determine their mineralogical composition. Intact specimens of each of the two fragments of painted-plaster were placed, without any preparation, into the sample holder and then onto a spinning stage in order to maximise the random orientation of mineral components, and then scanned at 40kV (using Cu K radiation) between 5 and 700 2θ (at a step size of 0.008). The results obtained from the analysis of each of the painted samples were compared with those provided by the computer's data base.

Gas Chromatography is the investigative technique that uses the different absorption rates of different compounds to identify a particular substance. **Gas Chromatography with Mass Spectroscopy (GC-MS)** is a term which encompasses a diverse and important group of investigative methods that permit the separation of the closely related components often found in complex mixtures; many of such separations are impossible by other means. However, gas chromatograms are unable to identify a substance conclusively unless the chromatograms have themselves been substantiated by additional analysis using known standards under the same conditions and on the same machine. GC-MS analytical equipment is widely used in the analysis of organic materials from archaeological sites (White, 1978; Mills & White, 1999; Colombini *et al.*, 1999 and Evershed *et al.*, 2003).

A Perkin Elmer AutoSystem XL Gas Chromatograph and TurboMass Spectrometer (GC-MS) was used on the two small fragments of painted wall-plaster found in a back filled trench from Wheeler's 1930-33 Verulamium excavations in an attempt to determine the nature of the binding material that might have been used to fix the pigment to the plaster. Minute samples (weighing <0.1g) from the two fragments of painted-plaster and placed respectively in two clean two-necked round-bottom flasks with 2 ml of

dichloromethane. Once the samples had dissolved, the flasks were transferred into a glass water bath which had been placed on top of a small laboratory hot plate and then inserted into a fume cupboard. It was important to exclude air from both flasks by flushing with inert nitrogen; the necks were sealed with rubber seals. Non-disposable needles were inserted into both seals to allow nitrogen to flow through the system. Then 50 µl of the mixture BSTFA (N,O-Bis[trimethylsilyl] trifluoroacetamide) and TMCS (trimethylchlorosilane), in a ratio of 99 : 1, were added to each sample. BSTFA is a powerful trimethylsilyl donor and the TMCS enhances the reactivity of the BSTFA with samples which are difficult to derivatise, especially when trying to ascertain what type of binding material, whether a wax or an oil, had been used in the preparation of ancient pigments.

To improve the efficiency of the derivatization reaction, the samples were heated at a temperature of 70°C for thirty minutes in the warmed water bath. Once the samples had evaporated, 0.05 µl of dichloromethane was added and the prepared sample was injected into a J&W Scientific DB-5MS capillary column (length 30m, internal diameter 0.25mm, film thickness 0.25 µm). A standard programme was used throughout the analysis: the Oven temperature was set at 50°C for 1 minute, then increased at 10°C per minute to a final temperature of 325°C, which was sustained for 15 minutes, the injection temperature was 250°C, and the flow rate of the helium carrier gas was 1.3 ml per minute. The samples were injected in splitless mode with a splitless time of 1 minute. The total time allowed for the process was within the range 38 to 50 minutes. The Mass Spectrometer was operated in Electron Impact mode with an ionisation energy of 70eV. Spectra were recorded using full scan mode over the range 40 to 620 m/z. Modern day samples of beeswax and linseed oil were prepared using the same methodology as those of the painted samples to be used as standards.

First reported in 1928 the **Raman** effect detects the interaction between the scattering of electromagnetic waves and the vibration modes of molecules. The advent of lasers has enabled the analytical capacity Raman Spectroscopy to be dramatically improved; the application of micro-Raman Laser Spectroscopy is now one of the major instruments for the absolutely non-destructive analysis of chemical, mineralogical, gemmological and other materials and is especially useful in the field of archaeology. Using this non-destructive technique the sample size can be as small as 1µm in diameter. However, its present high cost has limited availability to a relatively small number of institutions. A Renishaw RM1000 laser Raman microprobe, equipped with an argon ion laser (514.5 nm) was used in this study for additional sample characterisation of two pellets from Fishbourne Roman Palace at Kingston University (courtesy of Professor A. Rankin).

In a previous study, **X-ray Fluorescence Spectroscopy (XRF)** using a Cambridge Instruments AN10000 X-ray Spectrometer with a Philip PV9500 detector and with a 20v Rhodium X-ray tube was used to analyse a samples of Egyptian Blue pellets from excavations carried out at Fishbourne Roman Palace over the period 1997 to 1999, (Clegg & Freeman, 2003). The technique is relatively sensitive and is capable of detecting elements above sodium (Na) in the Periodic Table and is particularly useful for detecting heavy metal pollutants such as lead (Pb). XRF is widely used in archaeological research because of its ability to carry out accurate, non-destructive analyses at high speed, with the results being available within minutes (Skoog & Leary, 1992).

CHAPTER 4

Egyptian Blue Pellets, Fishbourne Roman Palace, Chichester

They vary greatly in tint ... some of a light and ... pure blue ...

W J Russell 1892, 46

4.1 Introduction

The building of Fishbourne Roman Palace, near Chichester, began following the Roman invasion of AD 43; it was occupied continuously from *ca.* AD 65 until its destruction by fire in the late third century. (The geographical position of the site of the Palace is shown on Map 2). The palace consisted of four residential wings placed around a large garden (figure 4.1a). The south wing ... *with its view across the secluded southern gardens* ... was the private living apartments of the occupants of the Palace, whereas part of the east wing and the north wing constituted a suite of luxurious rooms for visiting dignitaries Cunliffe (1998, 107). The Palace was richly decorated with *marble mouldings* ... (Cunliffe 1998, 40), fine wall paintings and mosaics.

As discussed in Chapter 2 Egyptian Blue was widely used by ancient artisans throughout the Roman world to decorate interior walls and has been found on many samples of blue painted-wall plaster. A fine example being a large fragment of a second century AD wall painting, found in the north wing of the Palace, showing a small figure standing in front of a colonnaded building with the sea in the background (figure 4.1b). It has been compared to a similar painting found at Stabiae (near Pompeii) and, according to Cunliffe may have

been painted by the same school of painters (1998). Twelve Egyptian Blue pellets were obtained from the 2002 excavation at Fishbourne Roman Palace. Ten of the pellets were found on spoil heaps by metal detectors and two were found in a ditch which pre-dated the proto-palace. They all varied in colour, shape, size and texture.

4.2 Analytical techniques used on these pellets

All the pellets were examined by LA-ICP-MS and SEM-EDAX in order to qualitatively determine their geochemical composition and classification. The samples were also examined under a MEIJI techno RZ zoom Stereomicroscope with a fibre-optic light source to study in fine detail their textural composition, structure and fabric. The methods used in the preparation of samples is discussed in Chapter 3. Because individual pellets are never homogeneous throughout, their described colours, identified with use of the Munsell Book of Color (Matt Finish Collection) 2001 should be considered as a guide only. The pellets were also weighed and measured as shown in figure 4.2.

4.3 Results

The elemental composition of each of the twelve pellets, as derived from LA-ICP-MS and SEM-EDAX analyses, is shown in the spectra of figure 4.3, and tabulated in figure 4.4. Chemical analysis of the Fishbourne Roman Palace pellets by LA-ICP-MS shows significant variation in the amounts of copper (Cu), iron (Fe) and tin (Sn) found in eleven of the pellets. Copper is, however, not detectable in one of the pellets, *viz.* FBE02 1005/14454. Calcium (Ca) was not recorded in any sample. Silica (Si) is one of the main components in the production of Egyptian Blue and was found in all the pellets with the exception of the following three, namely FBE02 1005/14448, FBE02 1139/17463 and FBE02 1145/17632. Carbon (C) was detected, in various amounts, in all of the

pellets; suggesting that the flux used in the production of these pellets was likely to have been potash.

The predominant isotope of lead (Pb) is 208. Unfortunately, some of the LA-ICP-MS spectra for this element did not demonstrate the presence of the three stable isotopes (*viz.* 206, 207 and 208) which are considered necessary before conclusive evidence of the presence of lead can be confirmed. On this basis lead was not identified in pellets FBE02 1013/14376, FBE02 1024/15353, FBE02 1139/17463 and FBE02 1145/17632 although it was present in all the other pellets.

Sodium (Na) was detected in eight of the pellets: FBE02 1005/14174, FBE02 1005/14448, FBE02 1006/16512, FBE02 1010/14932, FBE02 1013/14376, FBE02 1024/15353, FBE02 1139/17463 and FBE02 1145/17632 and may have been used as a flux in the manufacture of these pellets.

Aluminium (Al) was found in all the following pellets: FBE02 1005/14174, FBE02 1005/14454, FBE02 1005/14448, FBE02 1006/16512, FBE02 1010/14932, FBE02 1013/14376, FBE02 1024/15353, FBE02 1029/16203, FBE02 1071/17421(a), FBE02 1071/17421(b), FBE02 1139/17463 and FBE02 1145/17632.

Potassium (K) was detected in eleven of the pellets, namely: FBE02 1005/14174, FBE02 1005/14454, FBE02 1005/14448, FBE02 1006/16512, FBE02 1010/14932, FBE02 1013/14376, FBE02 1024/15353, FBE02 1071/17421(a), FBE02 1071/17421(b), FBE02 1139/17463 and FBE02 1145/17632. This suggests that potash was the flux used in the manufacture of these eleven pellets.

Barium (Ba) was identified in five of the pellets, namely: FBE02 1005/14454, FBE02 1006/16512, FBE02 1024/15453, FBE02 1029/16203 and FBE02 1145/17632.

All the pellets were, when originally excavated, covered by varying amounts of clayey soil. The underlying geology of the Fishbourne area is essentially London Clay (Eocene); the area represents the remains of an extensive coastal plain, with heavy clayey soils and rich organic deposits. Tertiary Clays and more recent soils, derived from estuarine alluvium, contain aluminium concentrations greater than 10% by weight and potassium concentrations greater than 2% by weight (Croudace & Cundy, 1995) as well as background levels of barium in the soil which range from 100 – 3000 ppm. The identification of these elements in the soil surrounding some of the pellets was, therefore, not unexpected.

The results of the SEM-EDAX analysis differ considerably from those of LA-ICP-MS analysis. The SEM-EDAX analysis shows that in all the samples silica is present with various quantities of calcium, copper, iron, and sodium. Differing amounts of carbon were also present, however, no carbon was found in pellet FBE02 1006/16512 although it was detected by the LA-ICP-MS. Aluminium was detected in all the pellets, as it was in the LA-ICP-MS analysis. Magnesium (Mg) was found in eight of the pellets, namely: FBE02 1005/14454, FBE02 1005/14448, FBE02 1006/16512, FBE02 1010/14932, FBE02 1013/14376, FBE02 1024/15453, FBE02 1029/16203 and FBE02 1139/17463. Tin, lead and barium is absent in all of the samples. In four of the pellets, *viz.* FBE02 1005/14454, FBE02 1005/14448, FBE02 1010/14932 and FBE02 1024/15353, titanium (Ti) is found. Potassium is found in six pellets, *viz.* FBE02 1005/14454, FBE02 1005/14448, FBE02 1006/16512, FBE02 1010/14932, FBE02 1024/15353 and FBE02 1145/17632.

Titanium, potassium, aluminium and magnesium are elements commonly found in soil samples. With the exception of one pellet (see above) they all contained carbon and this together with aluminium, magnesium and potassium may indicate the nature of the flux used in the manufacture of the pellets. The variations in the chemical composition of the pellets, while based on qualitative, rather than quantitative LA-ICP-MS and SEM-EDAX scans, indicate considerable heterogeneity as mentioned. This may be due to either the materials sourced to produce these pellets, *ie* the available ingredients, or to the actual extent of the mixing of those ingredients in the manufacturing process, or indeed to both factors.

4.4 Texture and structure of the pellets

The texture and structure of all twelve pellets were closely examined by the naked eye and also microscopically (magnification x 7.5), figure 4.5. As a result of this examination the pellets were categorized into four types, classified, for convenience, as Fishbourne Roman Palace (FRP) Types I, II, III, and IV, shown in Table 1 (Clegg *et al.*, 2006).

The structure and texture of each pellet results from the nature of the materials used and the way in which they have been prepared and combined. In extensive experiments conducted by the author the intimate relationship between the degree to which the ingredients have been ground and the resulting microscopic structure of the pellet is clearly identifiable. This work is discussed at length in Chapter 9. From these experiments it is possible, when looking microscopically, at a given pellet to be highly confident of the extent to which the ingredients have been ground and prepared. And it is on the basis of this work that the following classification of the Fishbourne Roman Palace pellets has been constructed.

The structure of FRP Type I pellets [FBE02 1010/14932, FBE02 1013/14376 and FBE02 1145/173632] are those in which the ingredients have been roughly ground. The quartz grains are large and there are few inclusions (figure 4.6 (a) – (c)). The composition of FRP Type II pellets [FBE02 1005/14448, FBE02 1071/17421(a), FBE02 1071/17421(b) and FBE02 1139/17463] is very different: these are the pellets in which the ingredients would have been finely ground, although some small inclusions are found (figures 4.5.(d) – (g)). The size of the quartz grains are smaller than those of FRP Type I. The FRP Type III pellets [FBE02 1006/16512, FBE02 1024/15353 and FBE02 1029/16203], (figures 4.5 (h) – (j)), varied slightly from those of Types I and II. Although the ingredients of these pellets would have been finely ground, a few large grains of quartz remained, but very few inclusions were seen. The ingredients of FRP Type IV pellets [FBE02 1005/14174, FBE02 1005/14454] were finely ground and there are no inclusions, as shown in figures 4.5 (k) – (l).

When the pellets were examined microscopically for fine detail it was noticeable that although the grains varied in size and colour they all appeared to have been ‘washed’ showing well defined, clean margins and minimal débris. This can be seen in FBE02 1071/17421(a) and FBE02 1139/17463 (both FRP Type II pellets) in figure 4.6. The ‘washed’ grains would indicate that Fishbourne Roman Palace’s pellets were made by an expert. These two pellets are similar in texture, structure and friability; however the size of their individual grains varies noticeably, as is shown in figure 4.6. This is demonstrated in the following analysis: a selection of the grains have had their long axis determined. From pellet FBE02 1071/17421(a) 25 grains were measured. The longest axis being 646.3 μm whilst the shortest was 258.5 μm ; the mean length was 464.9 μm with a standard deviation of 107.3 μm and a standard error of the mean of 21.9 μm . In contrast, the 21 measured grains of

pellet FBE02 1139/17463 showed a mean length of 593.9 μm with a standard deviation of 153.4 μm and a standard error of the mean of 34.3 μm . The longest axis measured was 850.1 μm and the shortest was 293.5 μm . Pellet FBE02 1071/17421(a) has a lower standard error of the mean and this supports the contention that the grains of this pellet have been sorted and washed to a greater degree than those of FBE02 1139/17463. The statistical analysis was conducted on only two of the pellets, both friable, from which grains were easily obtained. It may be concluded that these two (otherwise similar) pellets were made at different times and / or possibly by different operatives. It was not possible to obtain material suitable for analysis from any of the other pellets without exposing them to unacceptable damage.

In composition all twelve of the pellets show a smoothed, amorphous, glassy slag-type structure, possibly caused by high temperatures during the firing process. With the exception of FRP02 1071/17421(a), 4.7(i), which shows part of a large single prismatic crystal (the green colour shown is a construct) the SEM-EDAX images of the crystal habit of the pellets show an overall general uniformity - given the textural differences in the nature of the pellets. The crystal habit of the twelve pellets is shown in figure 4.7(a – l), where it can be seen that the damaged platy and tabular habit is predominant. Although some crystal habit is recognizable in all of the pellets, it is impossible to identify any particular mineral that may have been used in the manufacture of these pellets.

4.5 Discussion

The results of the LA-ICP-MS analysis show that calcium is lacking in all of the samples [which is actually in conformity with that the ‘recipe’ suggested by Vitruvius’s (Book VII, XI, 1)]. However, the presence of tin and, in the majority of pellets, lead, copper and iron is common to all but one of the samples, *viz.* (FBE02 1005/14454), raising the possibility that scrap metal, in particular

bronze scrap, was an important ingredient in the production of the Fishbourne Roman Palace pellets. Similar observations were made by Damiani *et al.*, (2003) when investigating the House of Diana at Costa, see Chapter 2.

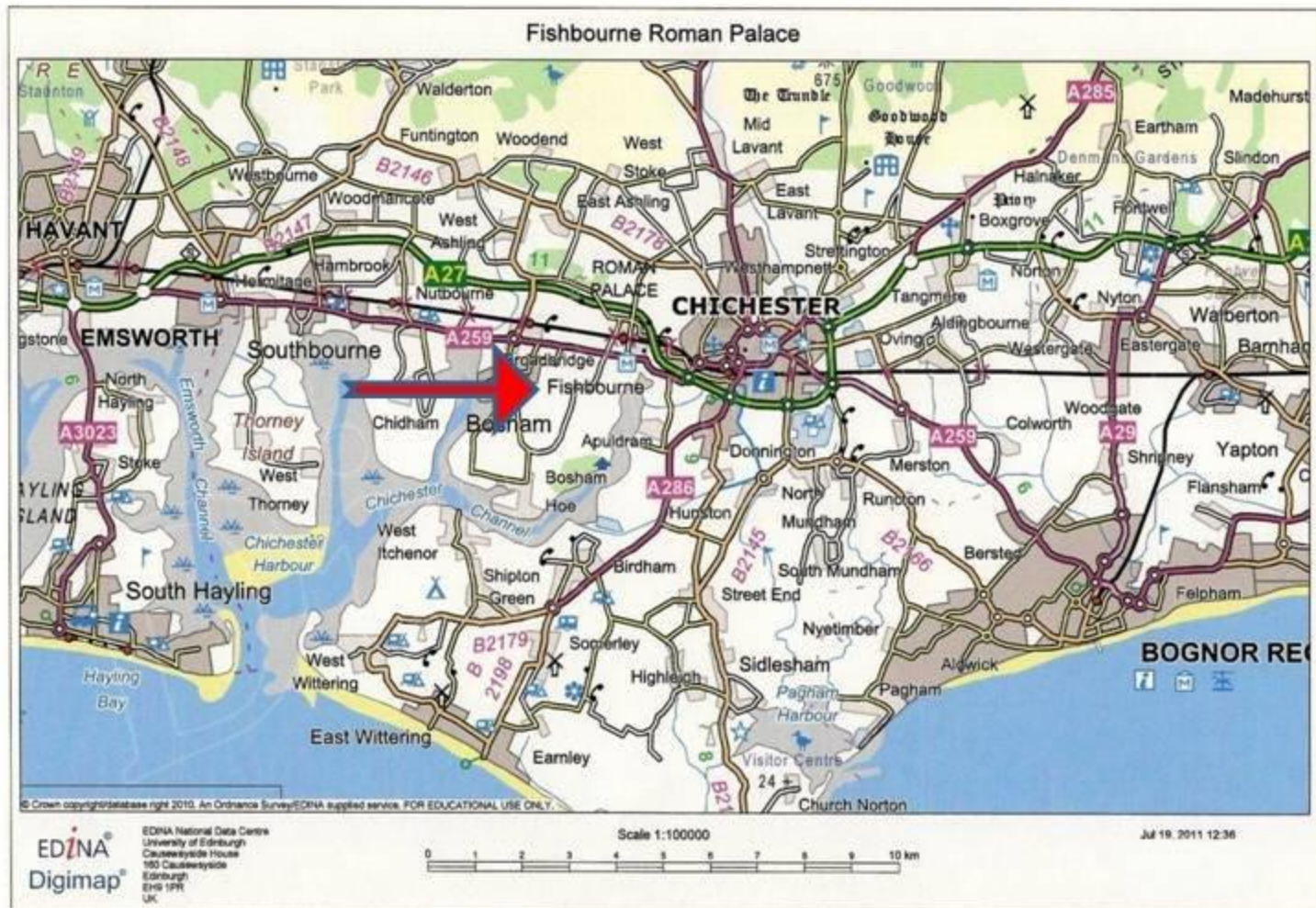
It is well established that iron is frequently associated with sand, (as an oxide or oxyhydroxide contaminate) which is one of the main ingredients in the production of Egyptian Blue pellets. The other ingredients for producing such pellets, using scrap metal, would have been readily available during the building of Fishbourne Roman Palace: during the excavation of the Palace evidence was found suggesting base foundations of Belgic-type kilns which may implies that, with all the different professional skills required to assemble such a grand structure, at least some of the pellets may have been produced locally, on site (Manley & Rudkin, 2006).

The results of the SEM-EDAX analysis, however, contradict the above hypothesis, that scrap metal was used, since neither tin or lead was identified. Calcium was positively identified, implying, incidentally, that Vitruvius's written recipe was not followed - it is assumed that the sand used by Vitruvius was 'contaminated' with lime, thus providing (unnoticed) one of the essential ingredients for the manufacture of Egyptian Blue pellets. Other, anachronistic elements were also identified. These elements, such as aluminium, titanium and magnesium are likely to be soil contaminants. Iron is frequently associated with silica. All the Fishbourne pellets were found isolated in a soil matrix.

On detailed examination the two Egyptian Blue pellets (FBE02 1071/17421(a) and FBE02 1139/17363), classified as FRP Type II (Table 1), were notably friable to touch and were clearly of a different texture and structure to all the other pellets found during the 2002 excavations. They correspond to the description given by Russell (1892, 46) ... *every specimen of the frits that I*

have seen has been in the friable condition ... [and] ...on rubbing they can be readily reduced to powder... It is unlikely, therefore, that these two pellets were made locally. Knowing that those who commissioned Fishbourne Roman Palace engaged master craftsmen (Cunliffe, 1998), most likely Roman-trained, then these two pellets could have been manufactured at a factory site such, as Vestorius' industrial plant in Puteoli, modern day Pozzuoli. Were this to be the case then these pellets would have been brought to Fishbourne by such a master craftsmen and his entourage and formed part of a larger batch of pellets and other pigments used to decorate the interior walls of the palace during its initial construction.

The two friable pellets, FBE02 1071/17421(a) and FBE02 1139/17363, were found in a very early ditch, pre-dating A.D 43. However, ... *that an amount of wall-painting may have been undertaken in the vicinity in the decades prior to AD 43 must, however, be treated with caution ...* (Clegg, 2005, 78) since painted plaster from such an early date is very rare in Roman Britain. During the 2002 excavations the bottom of this ditch was moist. And ... *the clay soils at Fishbourne are very conducive to small things becoming attached the soles of boots ... [of excavators, and] ... it is possible that these two finds could have become located in the ditch as a result of contamination* (Clegg, 2005, 78).



Map 2 showing site of Fishbourne Roman Palace, near Chichester in West Sussex

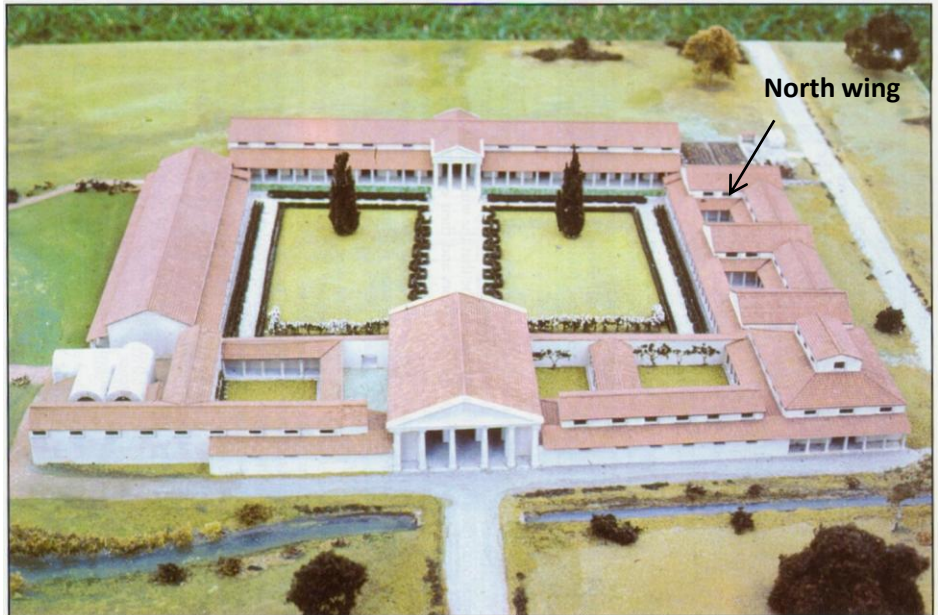


Figure 4.1a A model depicting Fishbourne Roman Palace, *ca* 1st century AD



Figure 4.1b Fragment of blue painted wall plaster painting showing the famous balcony scene.

Kind permission of Sussex Archaeological Society.

Figure 4.2 Showing weight, dimensions and colour



4.2a FBE02 1005/14174

Weight: 1.19g

Dimensions: 9.5 x 14mm

Munsell No. 10B 8/4



4.2b FBE02 1005/14454

Weight: 0.17g

Dimensions: 5 x 7 x 8mm

Munsell No. 10B 7/4



4.2c FBE02 1005/14448

Weight: 0.53g

Dimensions: 8 x 8 x 9mm

Munsell No. 10B 6/6



4.2d FBE02 1006/16512

Weight: 2.28g

Dimensions: 12 x 13 x 16 mm

Munsell No. 10B 7/6



4.2e FBE02 1010/14932

Weight: 1.95g

Dimensions: 13 x 15 x 18 mm

Munsell No. 10B 7/4



4.2. FBE02 1013/14376

Weight: 1.52g

Dimensions: 12 x 13 x 15 mm

Munsell No. 10B 7/6



4.2g FBE02 1024/15353

Weight: 0.71g

Dimensions: 8 x 10 x 12 mm

Munsell No. 10B 6/6



4.2h FBE02 1029/16203

Weight: 1.67g

Dimensions: 10 x 13 x 17 mm

Munsell No. 10B 6/6



4.2i FBE02 1071/17421 (a)

Weight: 12.09g

Dimensions: 21 x 26 x 31 mm

Munsell No. 5PB 5/8



4.2j FBE02 1071/17421 (b)

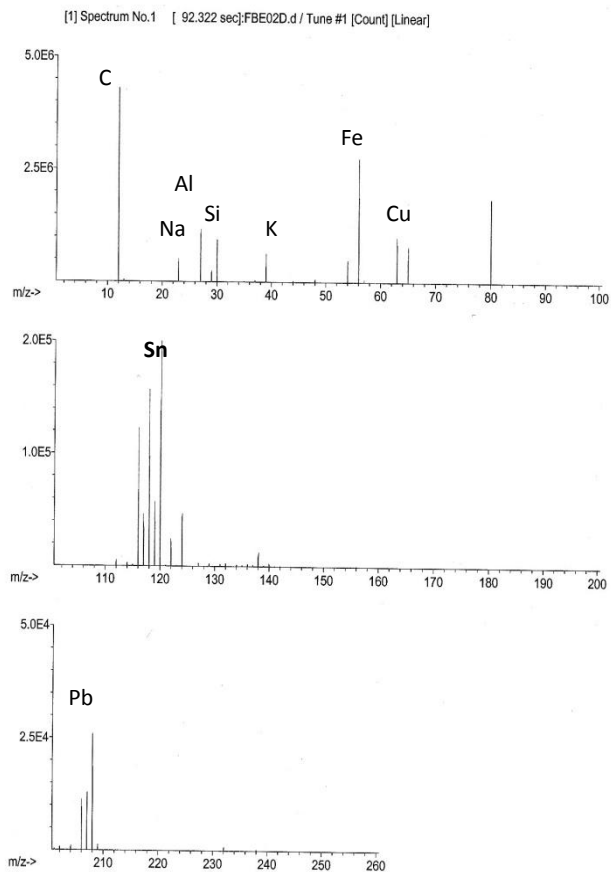
Weight: 17.62g

Dimensions: 15 x 32 x 40 mm

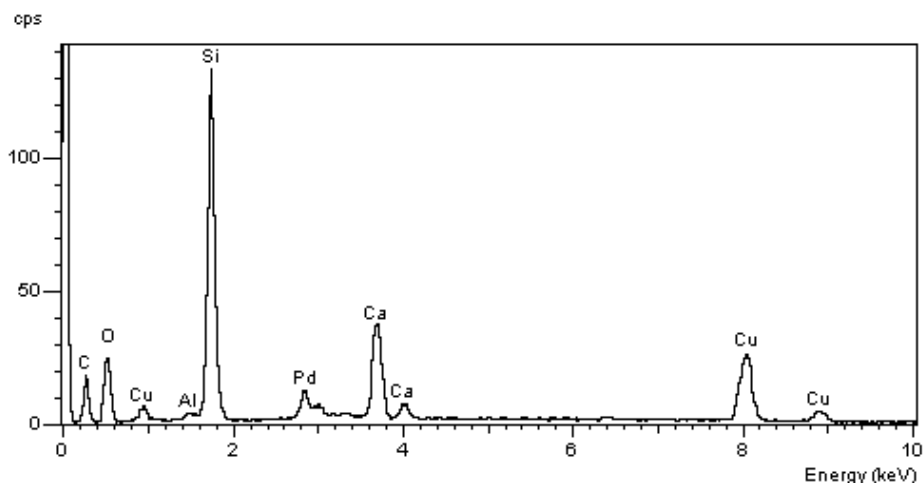
Munsell No. 5PB 6/8

Figure 4.3. Showing the LA-ICP-MS and SEM-EDAX results

(a) FBE02 1005/14174

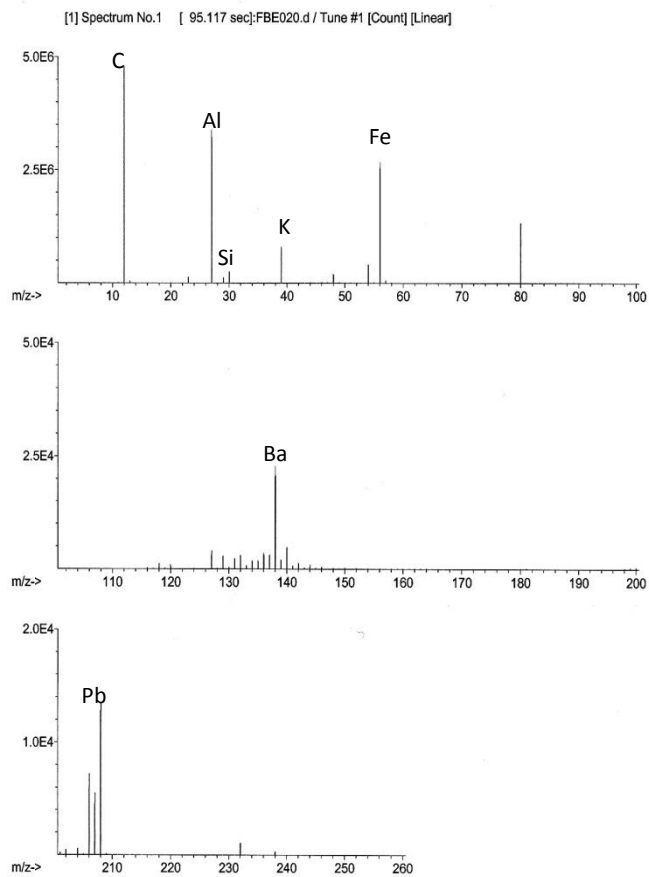


EDX energy spectrum for LA-ICP-MS

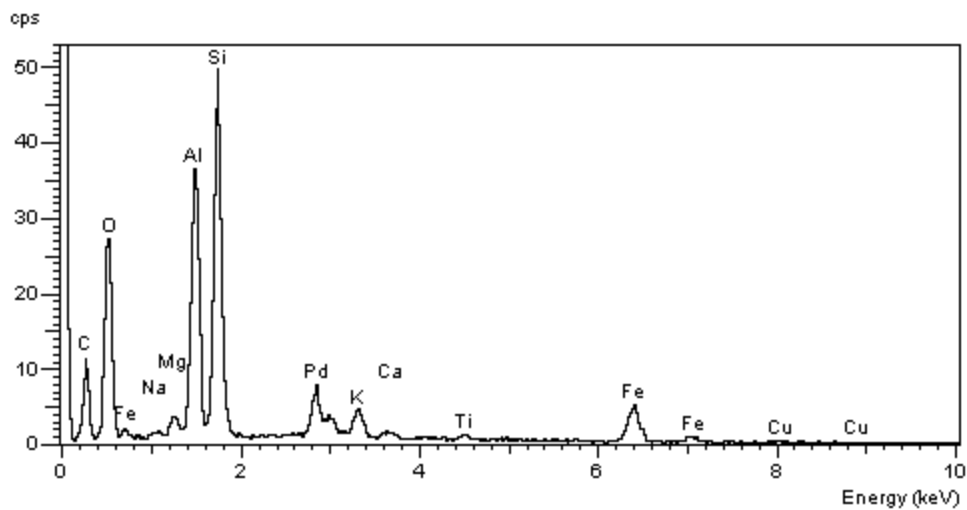


EDX energy spectrum for SEM-EDAX

(b) FBE02 1005/14454



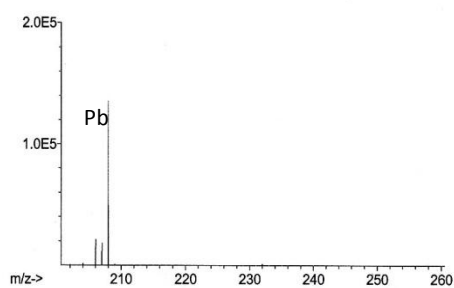
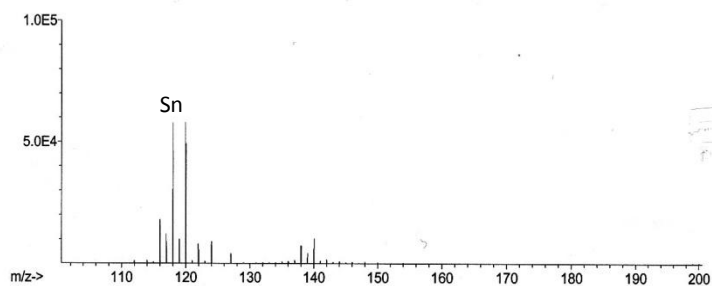
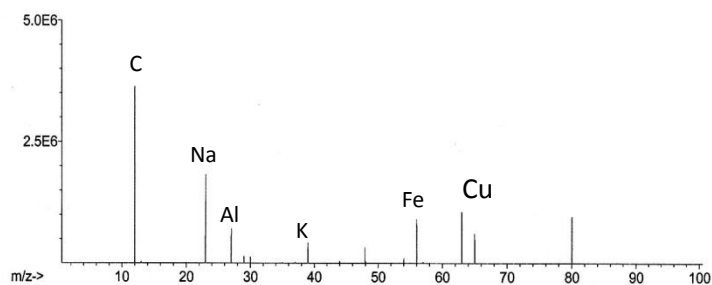
EDX energy spectrum for LA-ICP-MS



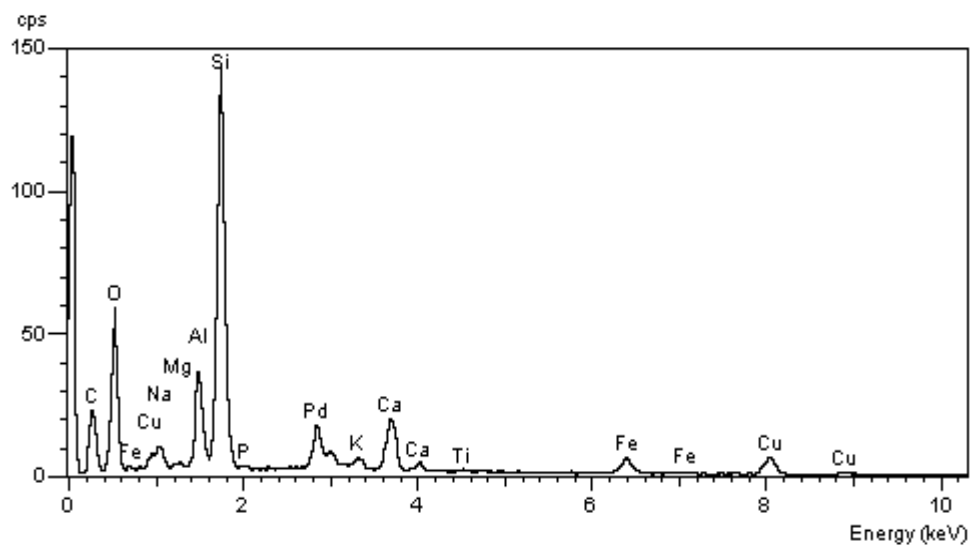
EDX energy spectrum for SEM-EDAX

(c) FBE02 1005/14448

[1] Spectrum No.1 [96.561 sec]:FBE02c.d / Tune #1 [Count] [Linear]

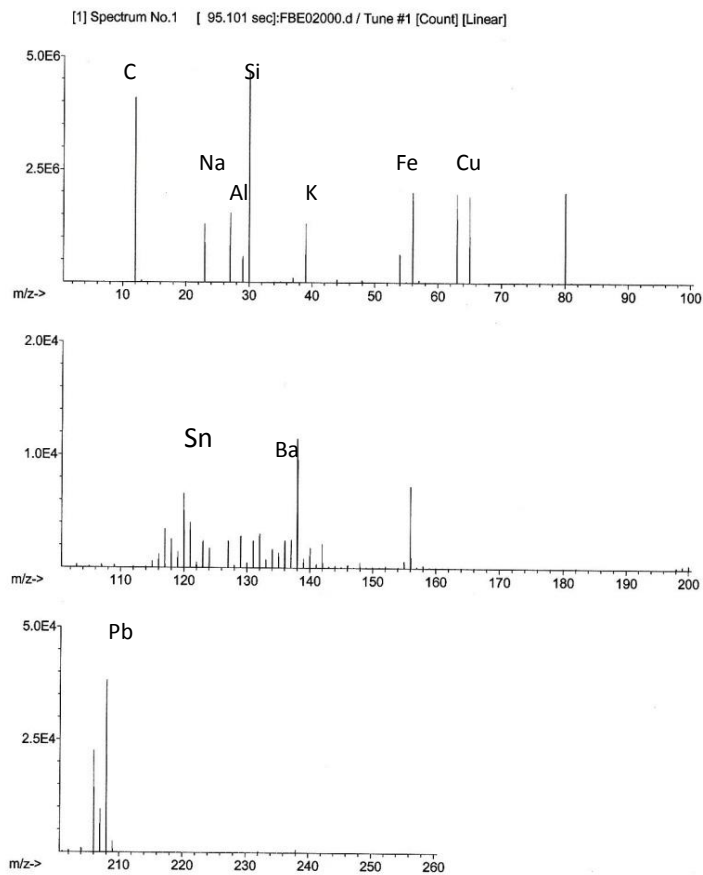


EDX energy spectrum for LA-ICP-MS spectra

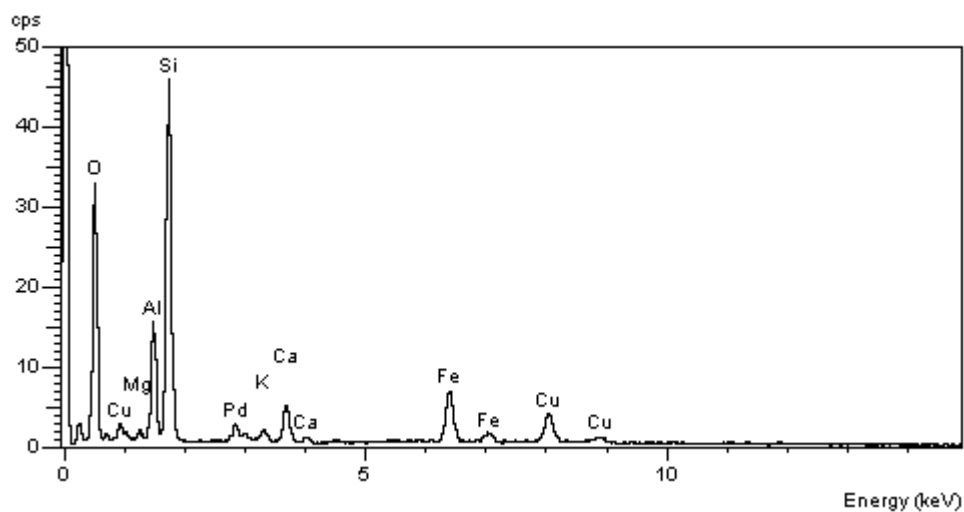


EDX energy spectrum for SEM-EDAX spectra

(d) FBE02 1006/16512

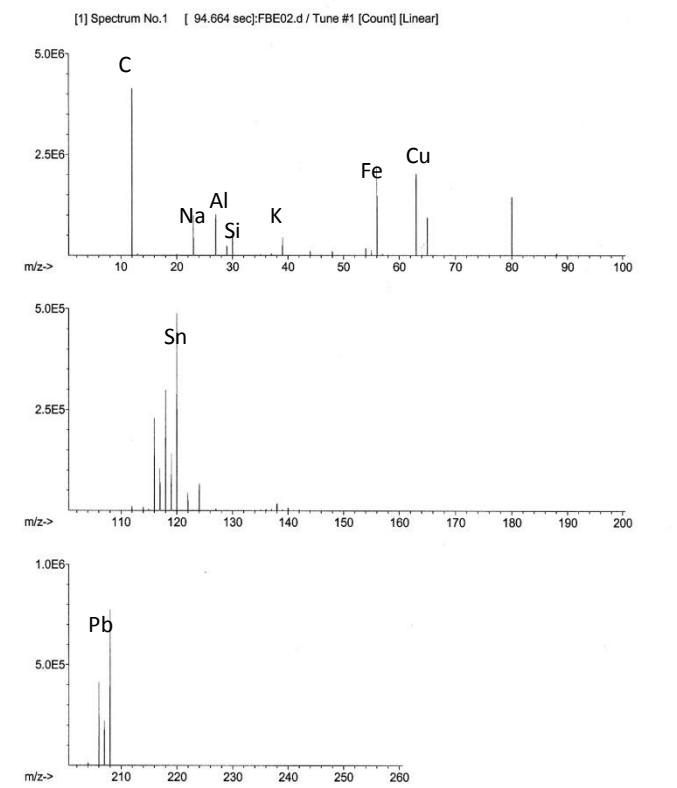


EDX energy spectrum from LA-ICP-MS spectra

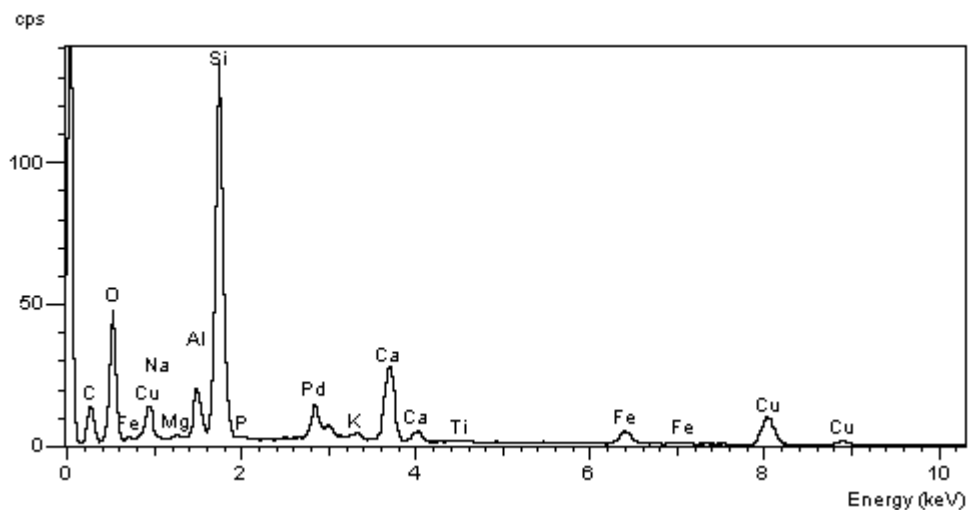


EDX energy spectrum from SEM-EDAX spectra

(e) FBE02 1010/14932

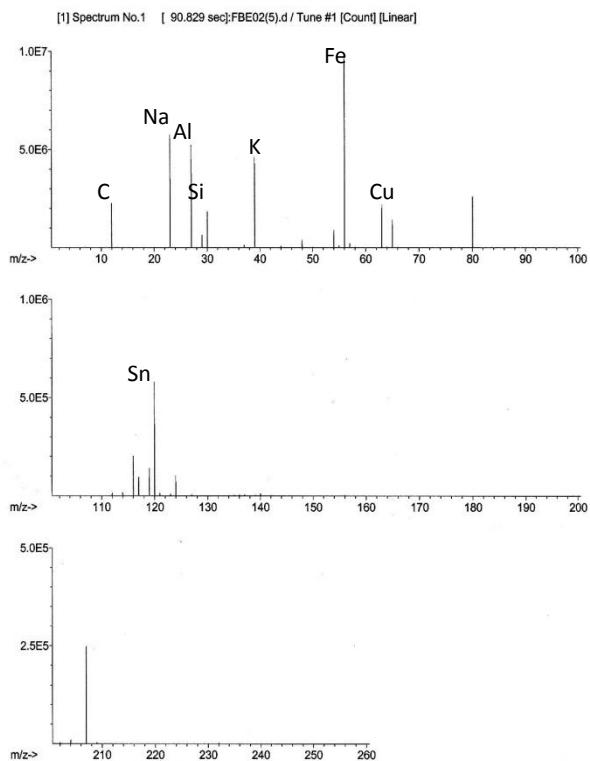


EDX energy spectrum from LA-ICP-MS spectra

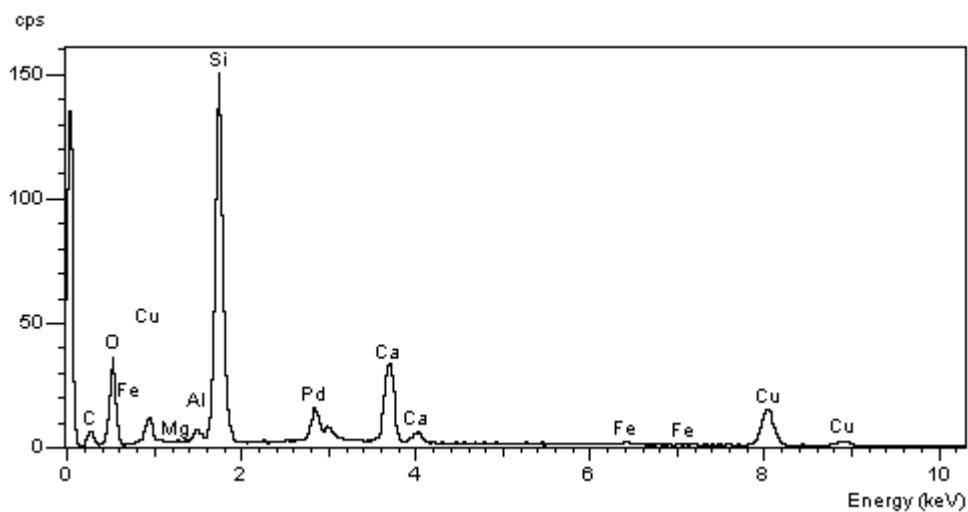


EDX energy spectrum from SEM-EDAX spectra

(f) FBE02 1013/14376

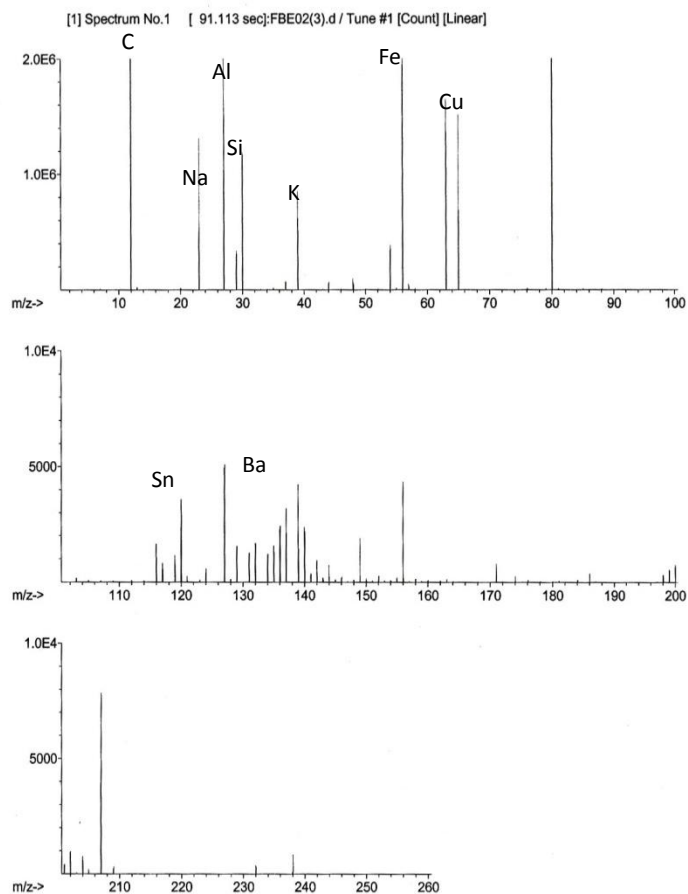


EDX energy spectrum from LA-ICP-MS spectra

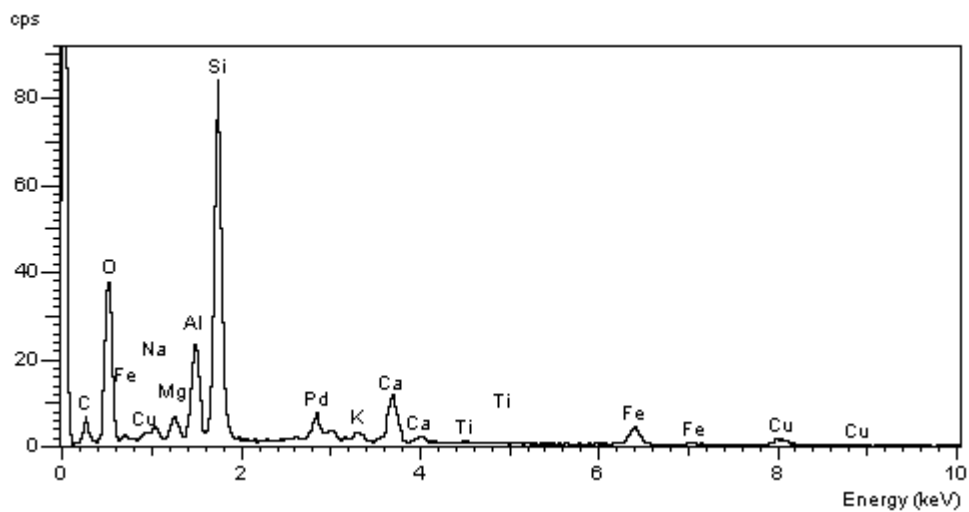


Energy spectrum from SEM-EDAX spectra

(g) FBE02 1024/15353

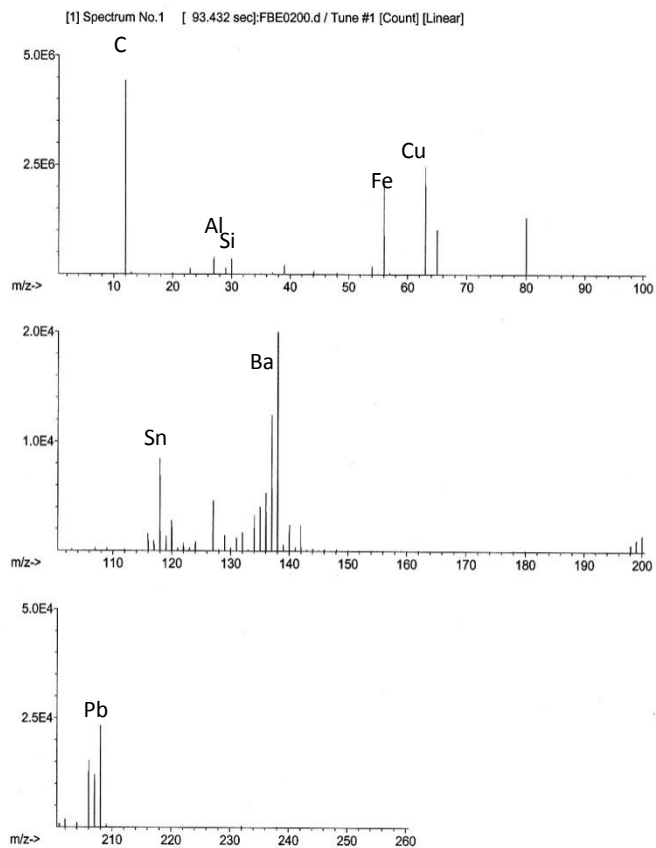


EDX energy spectrum from LA-ICP-MS spectra

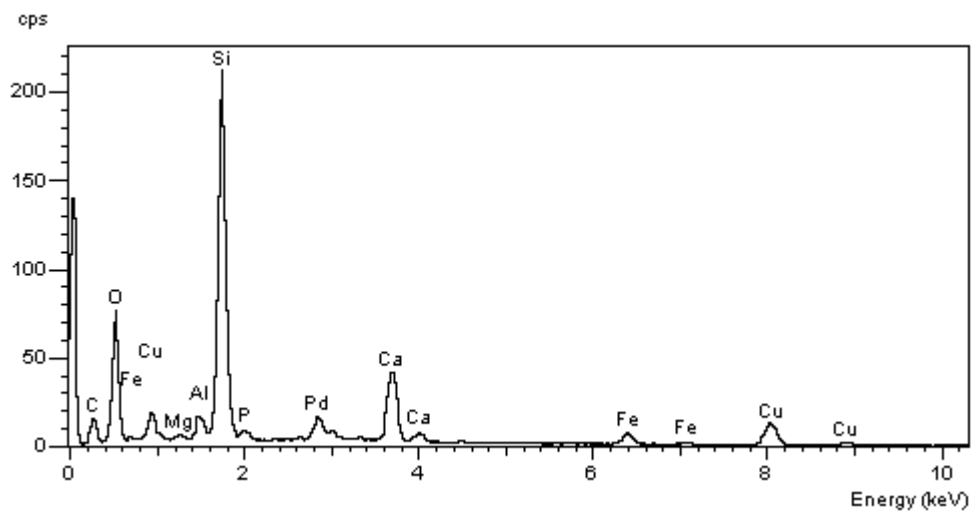


EDX energy spectrum from SEM-EDAX spectra

(h) FBE02 1029/116203

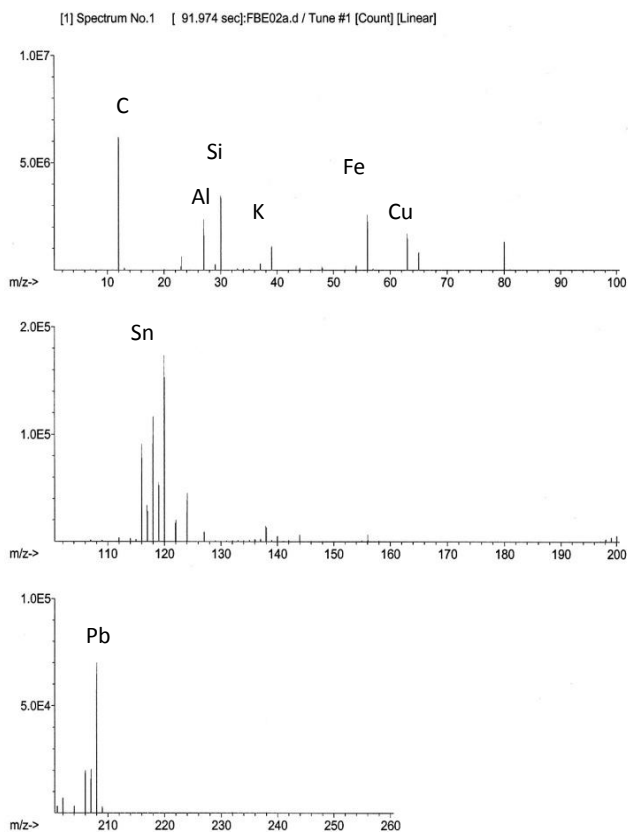


EDX spectrum from LA-ICP-MS spectra

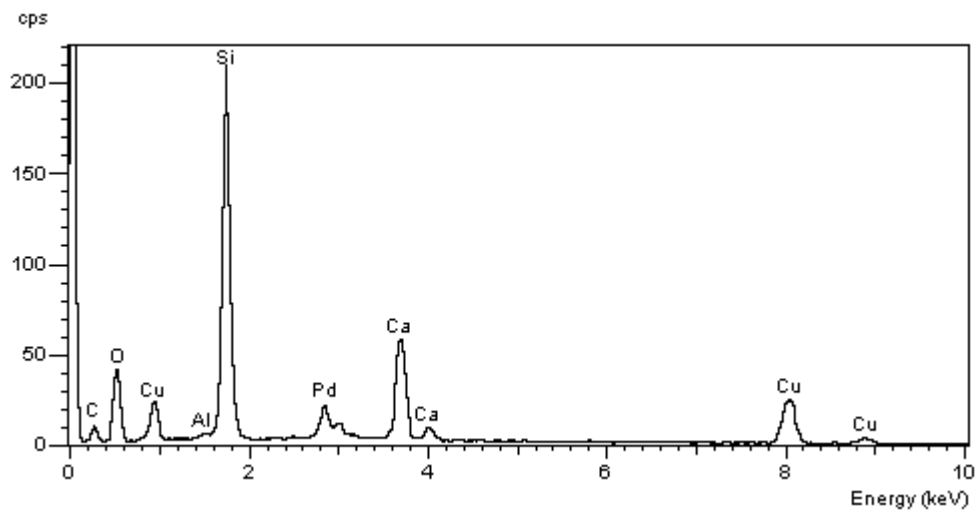


EDX spectrum from SEM-EDAX spectra

(i) FBE02 1071/17421 (a)

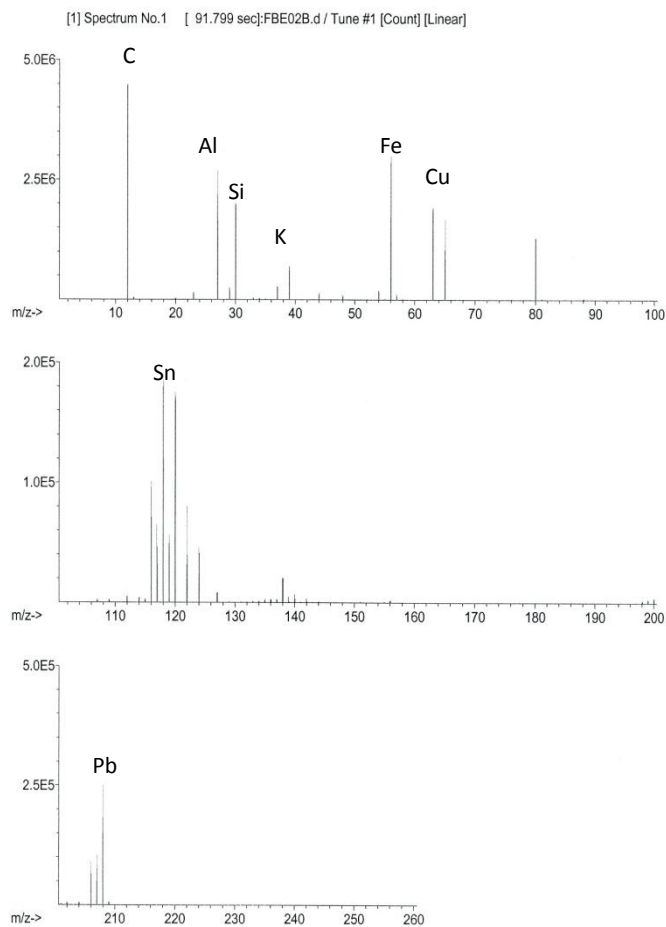


EDX energy spectrum from LA-ICP- MS spectra

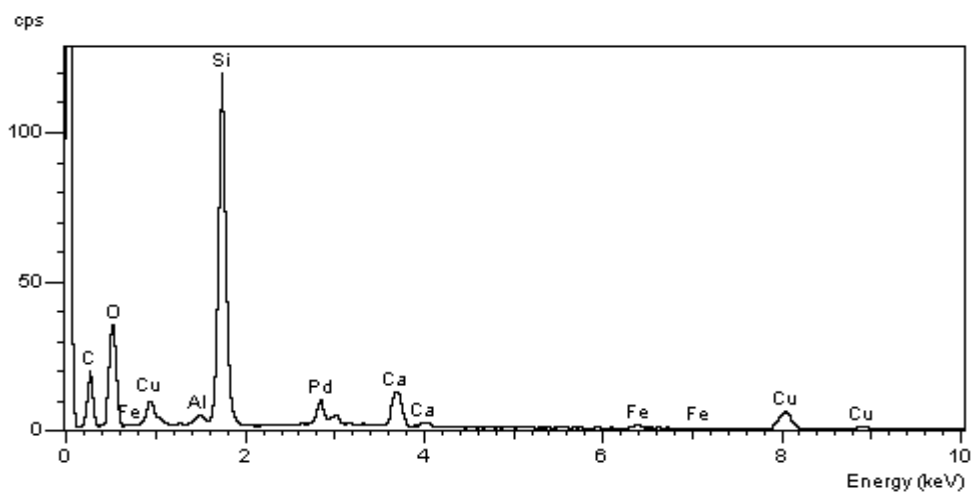


EDX energy spectrum from SEM-EDAX spectra

(j) FBE02 1071/17421 (b)

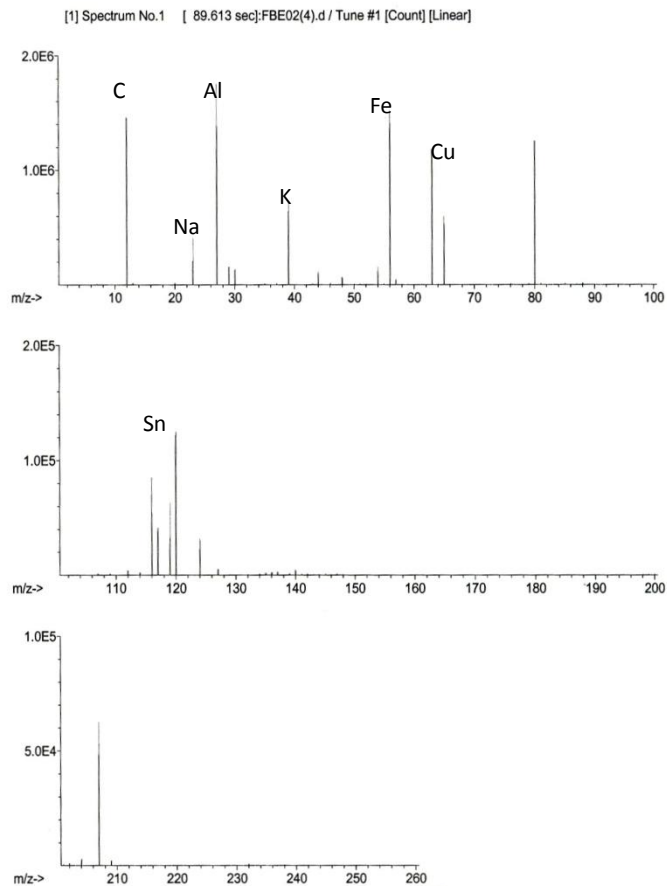


EDX energy spectrum from LA-ICP-MS spectra

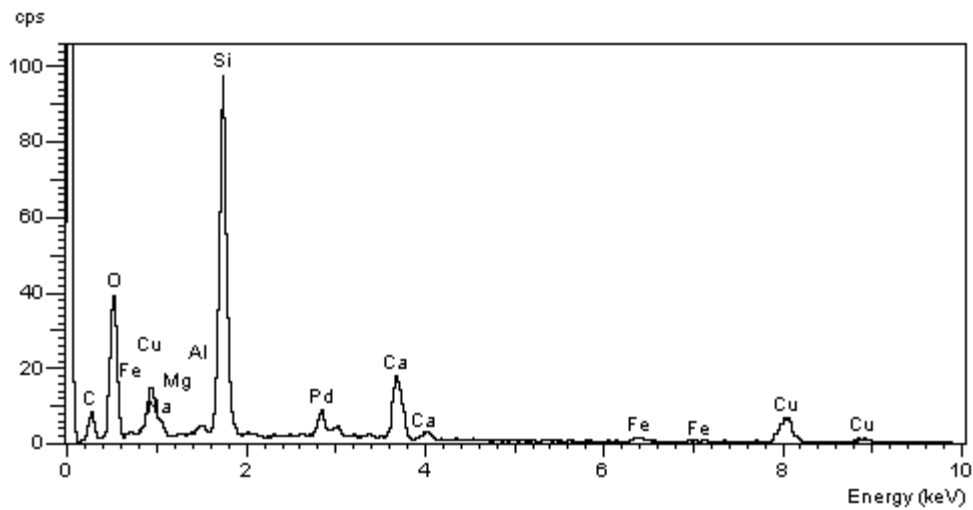


EDX energy spectrum from SEM-EDAX spectra

(k) FBE02 1139/17463

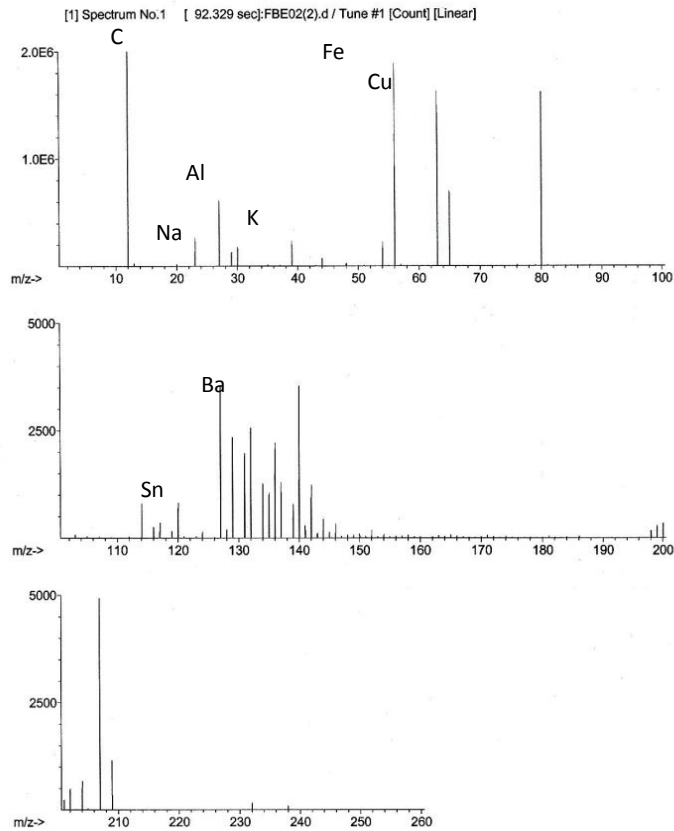


EDX energy spectrum from LA-ICP-MS spectra

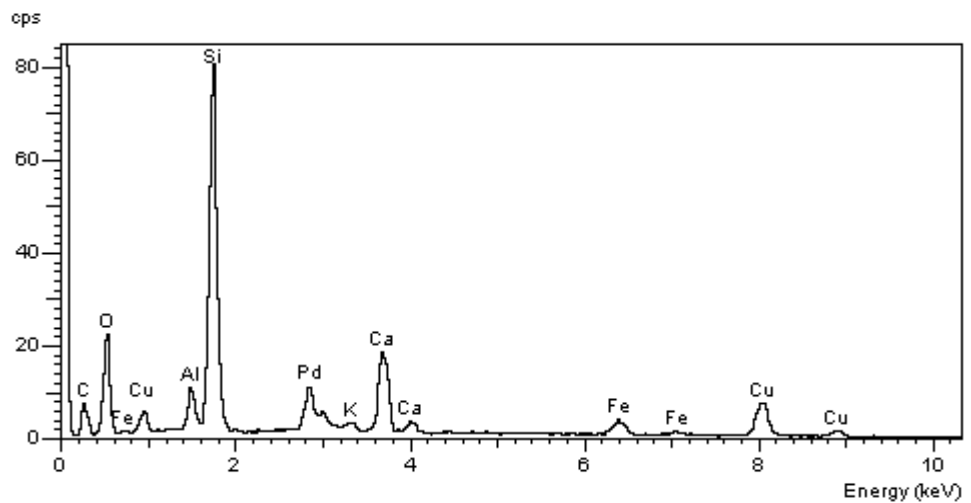


EDX energy spectrum from SEM-EDAX spectra

(I) FBE02 1145/17632



EDX energy spectrum from LA-ICP-MS spectra



EDX energy spectrum from SEM-EDAX spectra

Figure 4.4A

**Summary of elements detected by LA-ICP-MS Analysis of
Egyptian Blue pellets found at Fishbourne Roman Palace**

| | C | Cu | Fe | Si | Pb | Sb | Ni | Na | Ca | Ba | K | Al | Mg |
|-------------|---|----|----|----|----|----|----|----|----|----|---|----|----|
| FBE02 | | | | | | | | | | | | | |
| 1005/14174 | x | x | x | x | x | x | x | x | | | x | x | |
| FBE02 | | | | | | | | | | | | | |
| 1005/14454 | x | | x | x | x | | | | | x | x | x | |
| FBE02 | | | | | | | | | | | | | |
| 1005/14448 | x | x | x | | x | x | x | | | | x | x | |
| FBE02 | | | | | | | | | | | | | |
| 1006/16512 | x | x | x | x | x | x | x | | | x | x | x | |
| FBE02 | | | | | | | | | | | | | |
| 1010/14932 | x | x | x | x | x | x | x | | | | x | x | |
| FBE02 | | | | | | | | | | | | | |
| 1013/14376 | x | x | x | x | | x | x | | | | x | x | |
| FBE02 | | | | | | | | | | | | | |
| 1024/15353 | x | x | x | x | | x | x | | | x | x | x | |
| FBE02 | | | | | | | | | | | | | |
| 1029/116203 | x | x | x | x | x | x | | | | x | | x | |
| FBE02 | | | | | | | | | | | | | |
| 1071/17421a | x | x | x | x | x | x | | | | | x | x | |
| FBE02 | | | | | | | | | | | | | |
| 1071/17421b | x | x | x | x | x | x | | | | | x | x | |
| FBE02 | | | | | | | | | | | | | |
| 1139/17463 | x | x | x | | | x | x | | | | x | x | |
| FBE02 | | | | | | | | | | | | | |
| 1145/17632 | x | x | x | | | x | x | | | x | x | x | |

| | | | | |
|--------------|----|---------|----|-----------|
| KEY : | C | Carbo | N | |
| | C | n | a | Sodium |
| | Cu | Coppe | C | |
| | F | r | a | Calcium |
| | e | Iron | Ba | Bariu |
| | Si | Silicon | K | m |
| | P | | | Potassium |
| | b | Lead | Al | Aluminium |
| | S | Ti | M | |
| | n | n | g | Magnesium |

Figure 4.4B

**Summary of elements detected by SEM-EDAX Analysis of
Egyptian Blue pellets found at Fishbourne Roman Palace**

| | C | Cu | Fe | Si | Pb | Sn | Na | Ca | Ba | K | Al | Mg | Ti |
|----------------------|---|----|----|----|----|----|----|----|----|---|----|----|----|
| FBE02 1005/14174 | x | x | | x | | | | x | | | x | | |
| FBE02 1005/14454 | x | x | x | x | | | x | x | | x | x | x | x |
| FBE02 1005/14448 | x | x | x | x | | | x | x | | x | x | x | x |
| FBE02 1006/16512 | | x | x | x | | | | x | | x | x | x | |
| FBE02 1010/14932 | x | x | x | x | | | x | x | | x | x | x | x |
| FBE02 1013/14376 | x | x | x | x | | | | x | | | x | x | |
| FBE02 1024/15353 | x | x | x | x | | | x | x | | x | x | x | x |
| FBE02 1029/116203 | x | x | x | x | | | | x | | | x | x | |
| FBE02 1071/17421a | x | x | | x | | | | x | | | x | | |
| FBE02 1071/17421b | x | x | x | x | | | | x | | | x | | |
| FBE02 1139/17463 | x | x | x | x | | | x | x | | | x | x | |
| FBE02 1145/17632 | x | x | x | x | | | | x | | x | x | | |

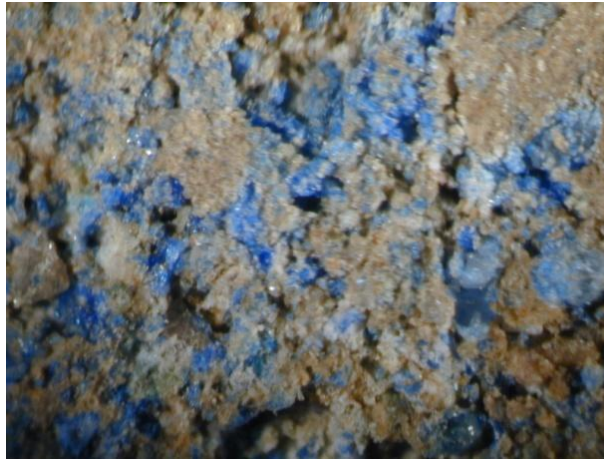
| | | | | |
|--------------|----|---------|----|-----------|
| KEY : | C | Carbon | Na | Sodium |
| | Cu | Copper | Ca | Calcium |
| | Fe | Iron | Ba | Barium |
| | Si | Silicon | K | Potassium |
| | Pb | Lead | Al | Aluminium |
| | Sn | Tin | Mg | Magnesium |
| | | | Ti | Titanium |

Table One. Showing the Classification of the twelve Fishbourne Roman Palace pellets.

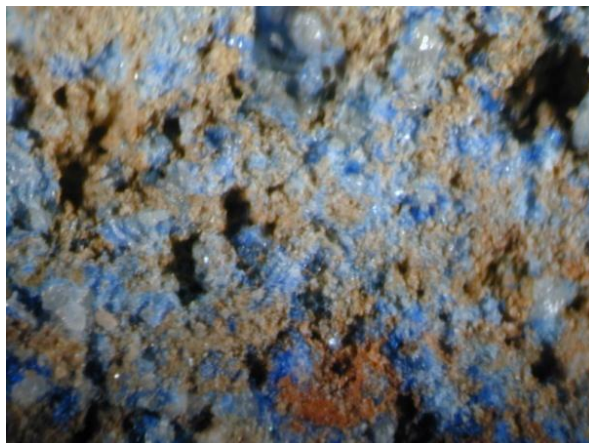
| <u>Group</u> | <u>Sample ID</u> |
|---------------------|--|
| FRP Type I | FBE02 1010/14932 FBE02 1013/14376 FBE02 1145/173632 |
| FRP Type II | FBE02 1005/14448 FBE02 1071/17421(a) FBE02 1071/17421(b) FBE02 1139/17463 |
| FRP Type III | FBE02 1006/16512 FBE02 1024/15353 FBE02 1029/16203 |
| FRP Type IV | FBE02 1005/14174 FBE02 1005/14454 |

Figure 4.5 Classification of Fishbourne Roman Palace's pellets

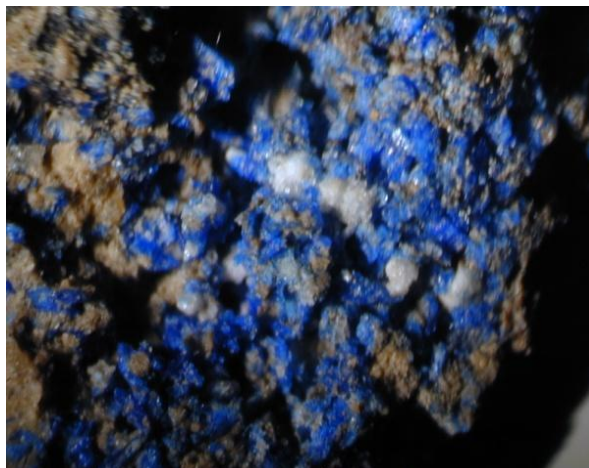
FRP Type I pellets



FBE02 1010/14932



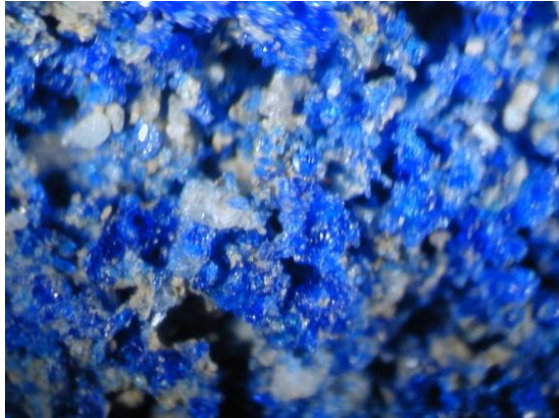
FBE02 1013/14376



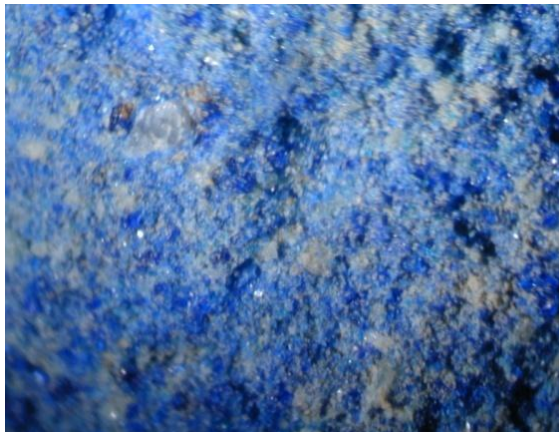
FBE02 1145/17632

FRP Type II pellets

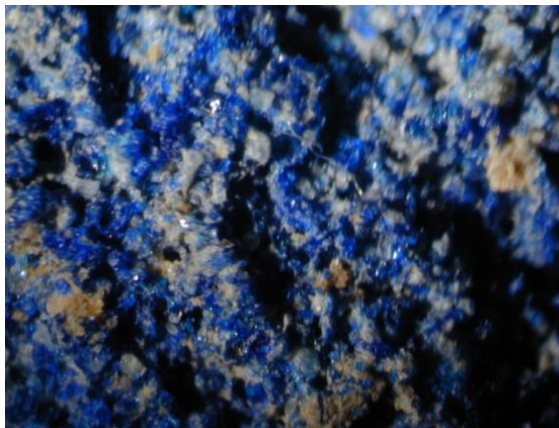
FBE02 1005/14448



FBE02 1071/17421 (a)



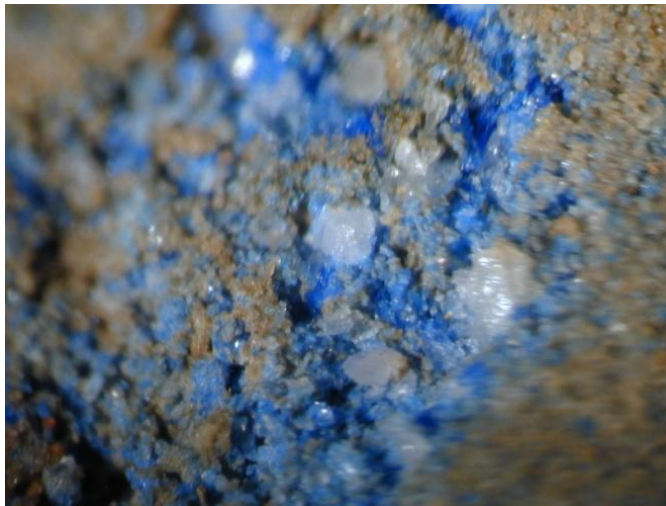
FBE02 1071/17421 (b)



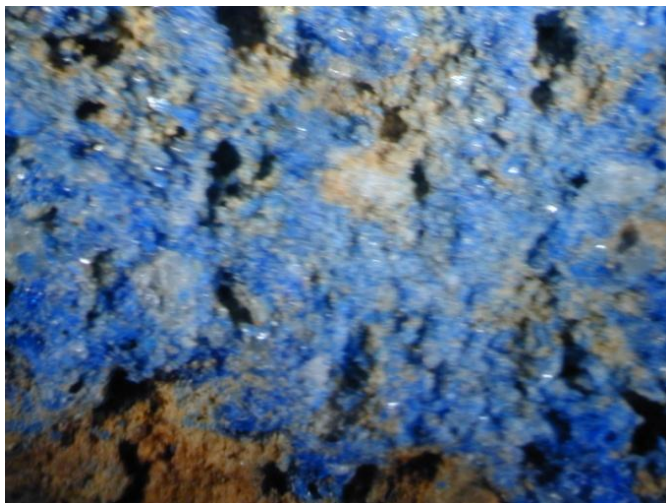
FBE02 1130/17463

FRP Type III pellets

FBE02 1006/16512

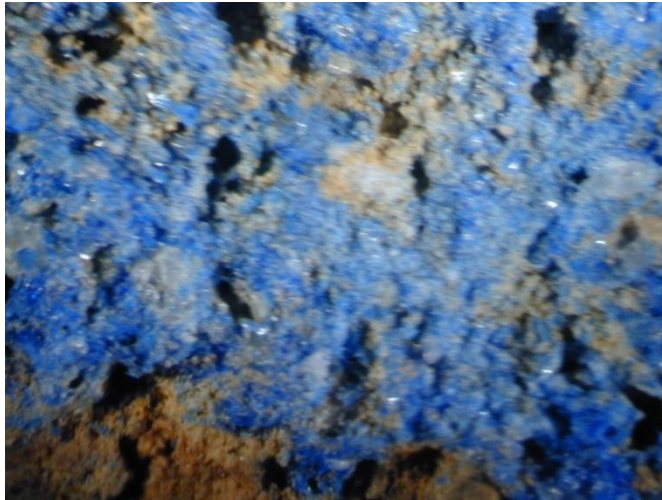


FBE02 1024/15353



FBE02 1029/16203

FRP Type IV pellets

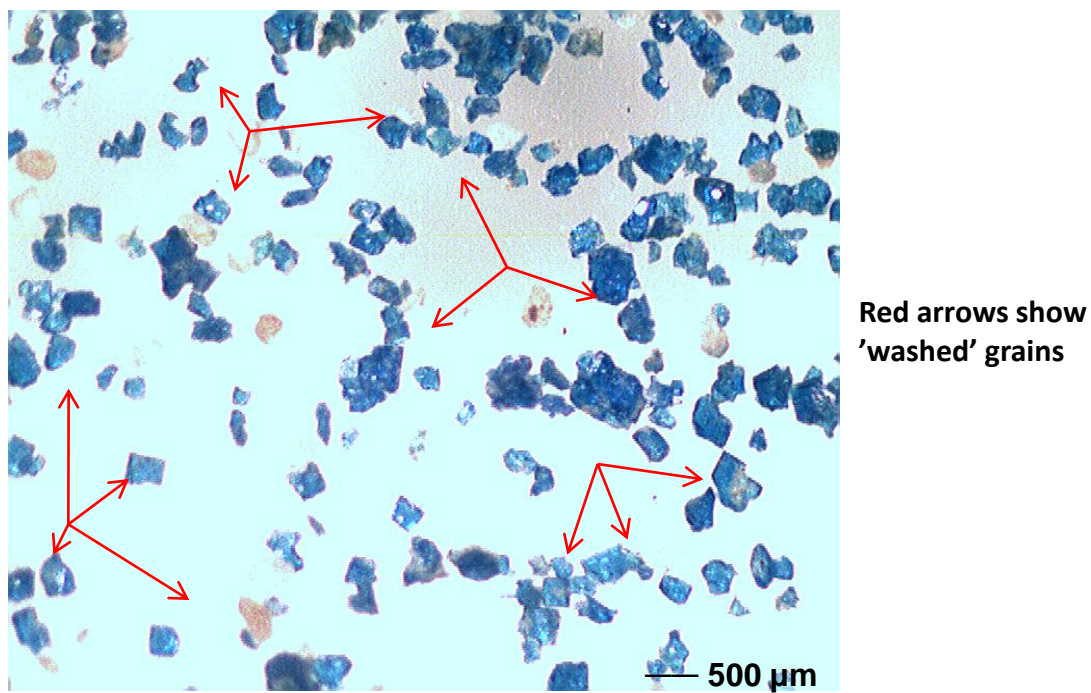


FBE02 1005/14174

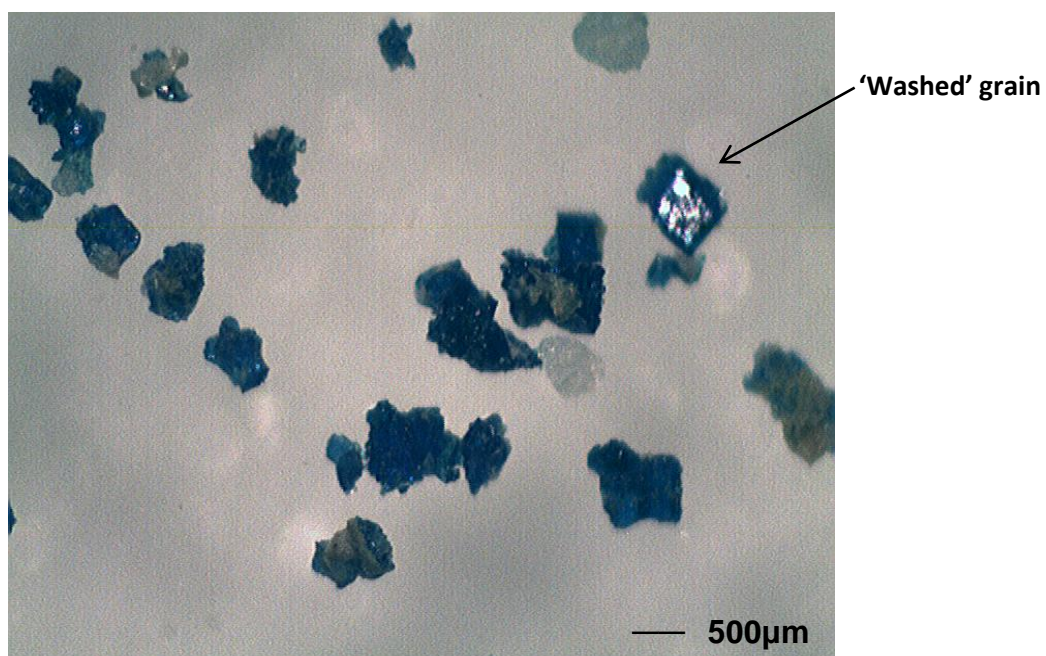


FBE02 1005/14454

Figure 4.6 An example of the grain structure of the pellets from Fishbourne Roman Palace

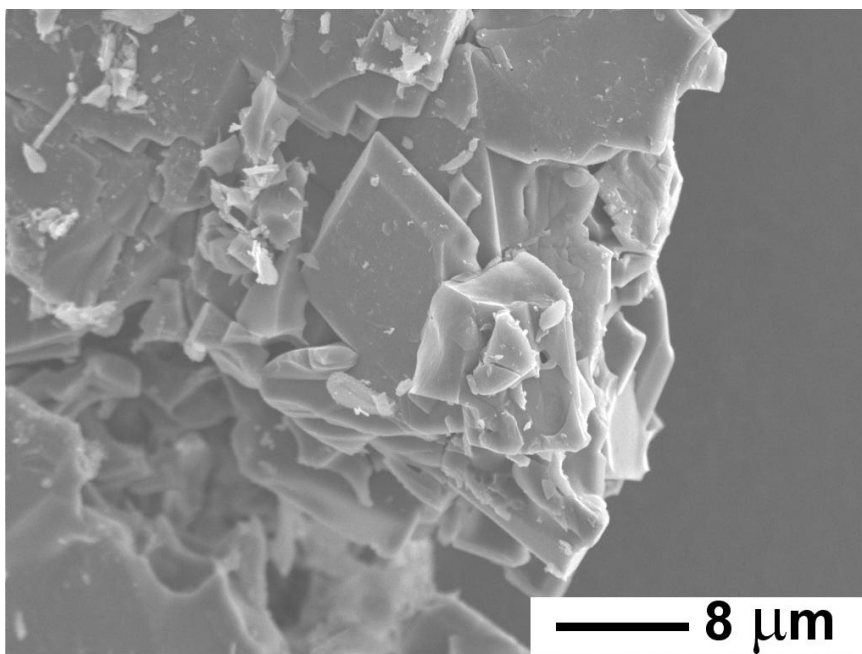


FBE02 1071/17421 (a)

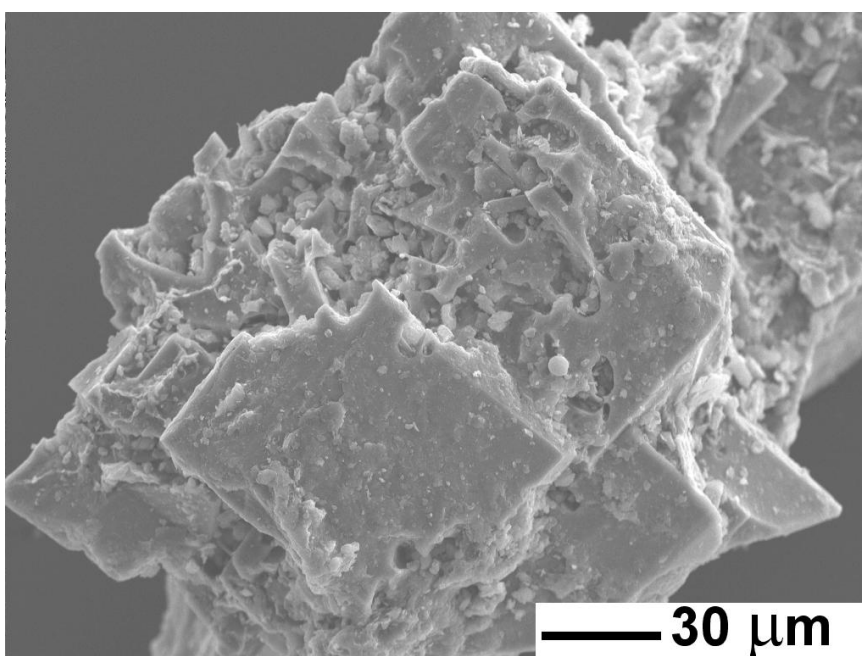


FBE02 1139/17463

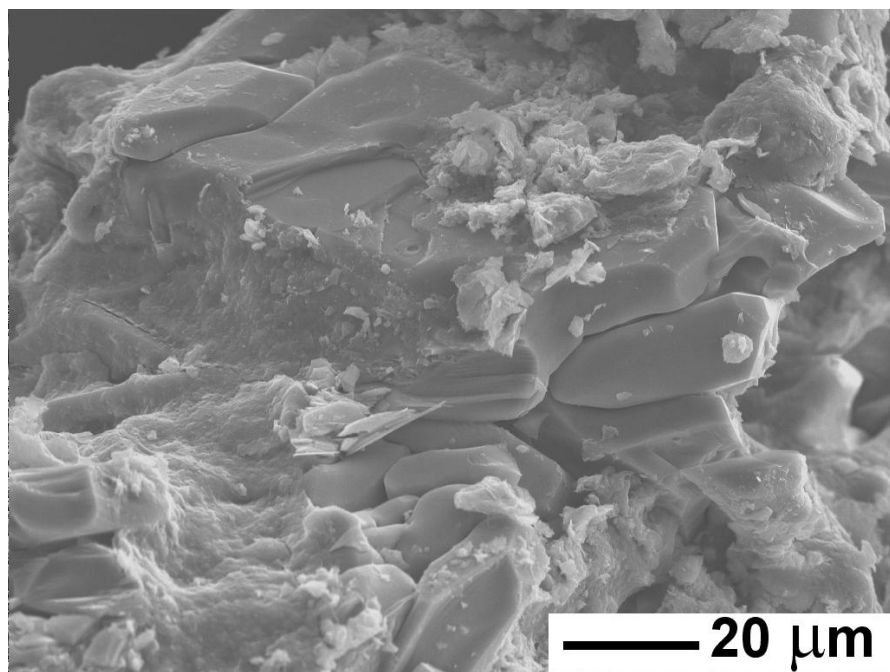
Figure 4.7 Showing the crystal habit of the twelve pellets from Fishbourne Roman Palace



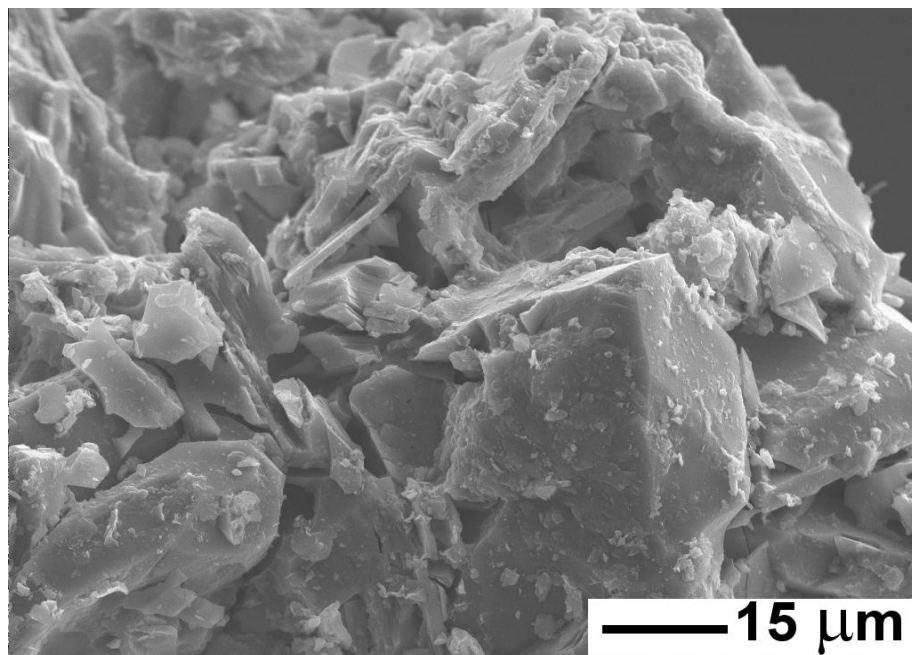
(a) FRP02 1005/14174: showing an agglomeration of tabular crystals



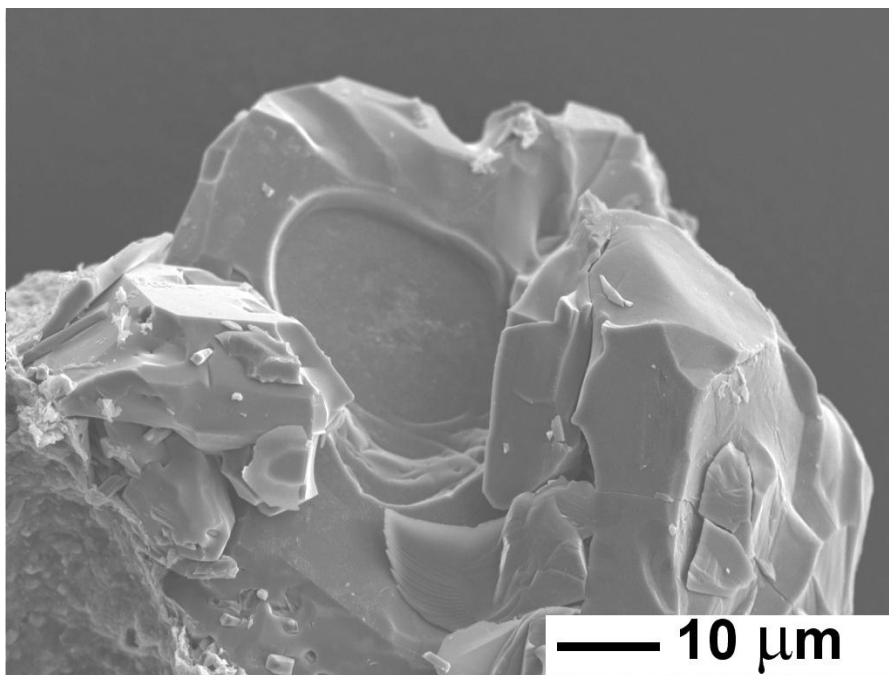
(b) FRP02 1005/14454: showing an agglomeration of fractured tabular crystals



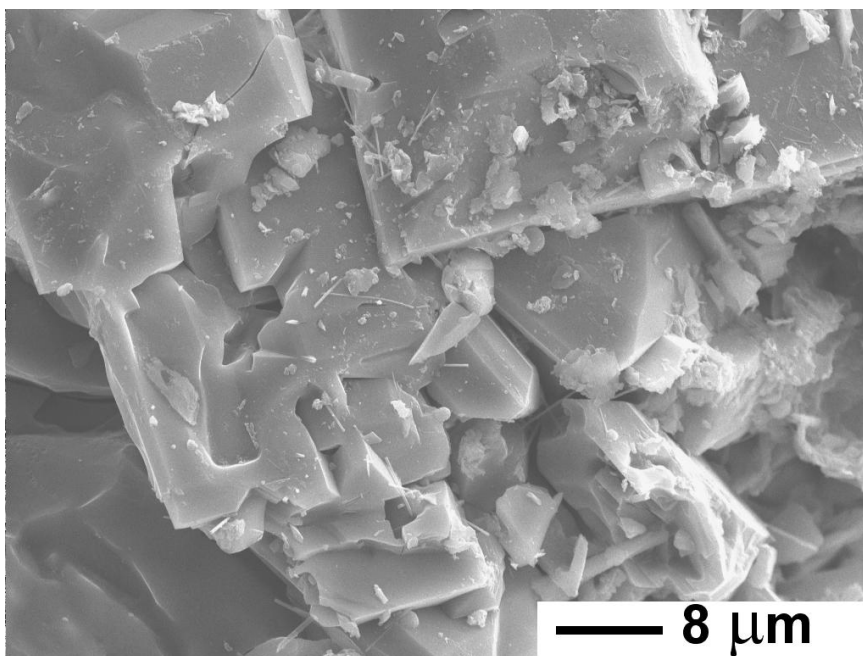
(c) FRP02 1005/14448: showing an agglomeration of tabular, platy and pyramidal crystals



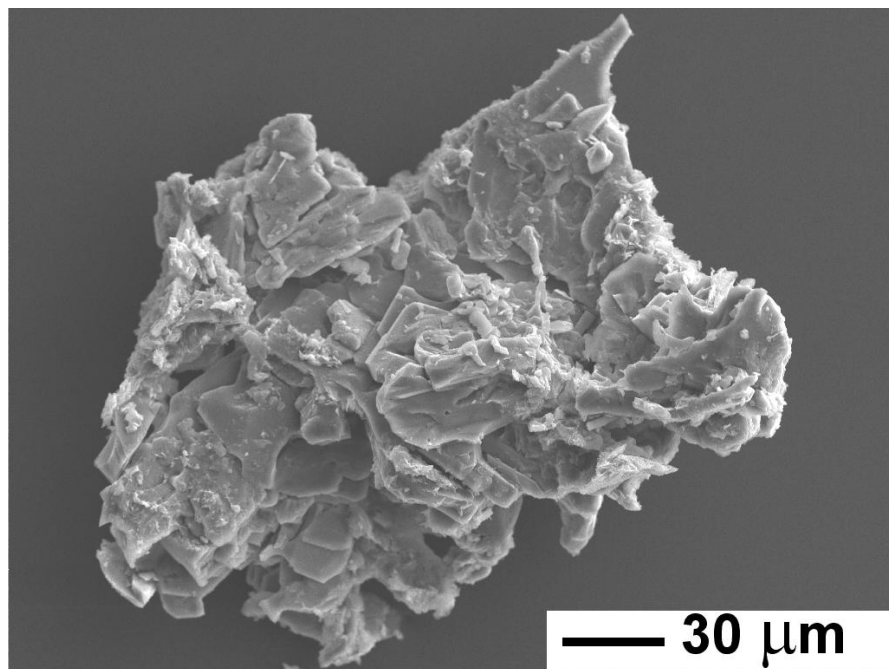
(d) FRP02 1006/16512: showing an agglomeration of fractured platy, tabular and pyramidal crystals



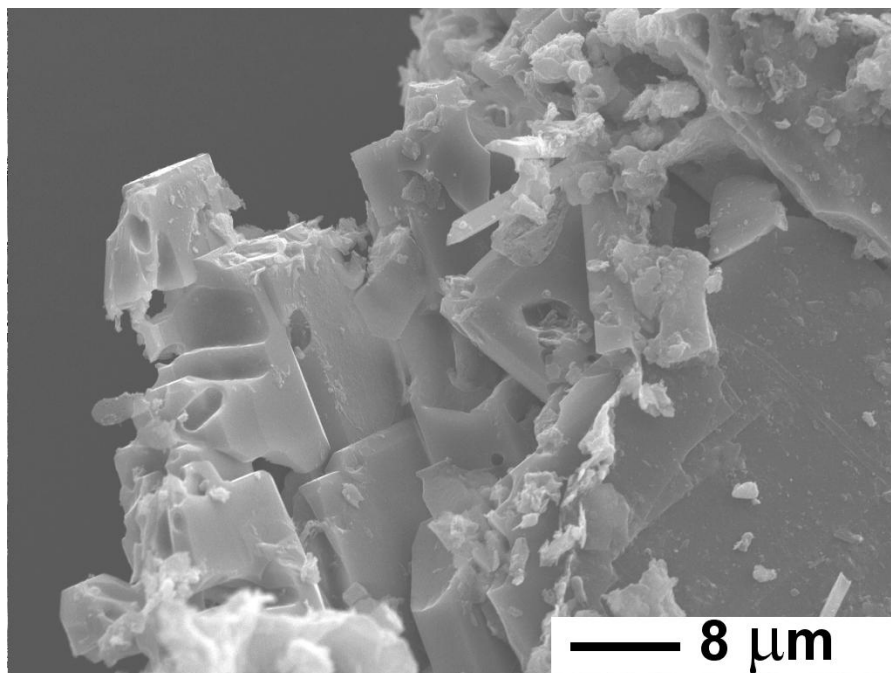
(e) FRP02 1010/19432: showing an agglomeration of fractured cubic and prismatic crystals



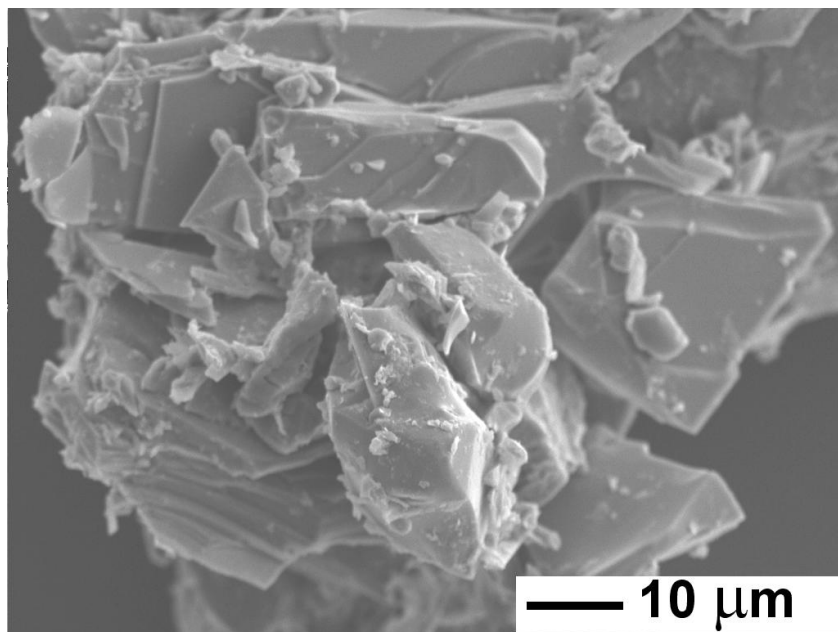
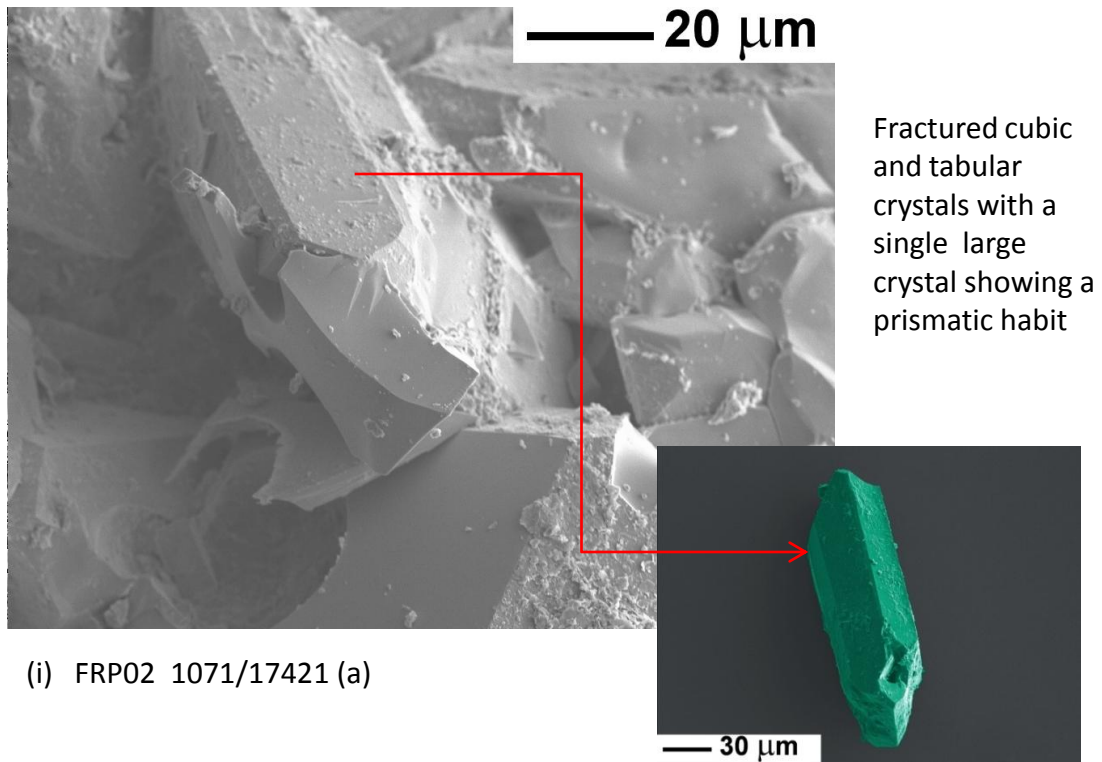
(f) FRP02 1013/14376: showing an agglomeration of platy, tabular, prismatic and cubic crystals

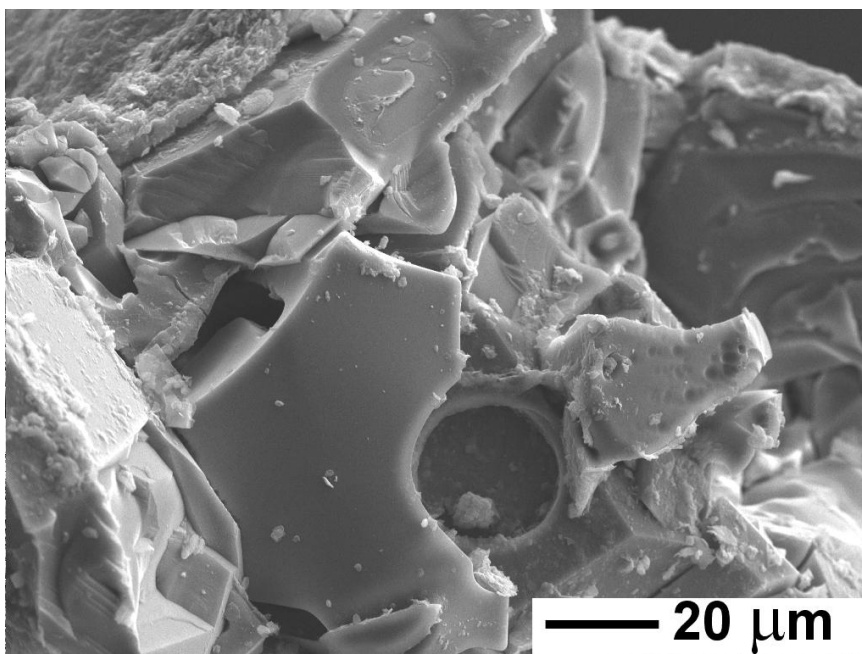


(g) FRP02 1024/15353: showing an agglomeration of fractured platy and tabular crystals

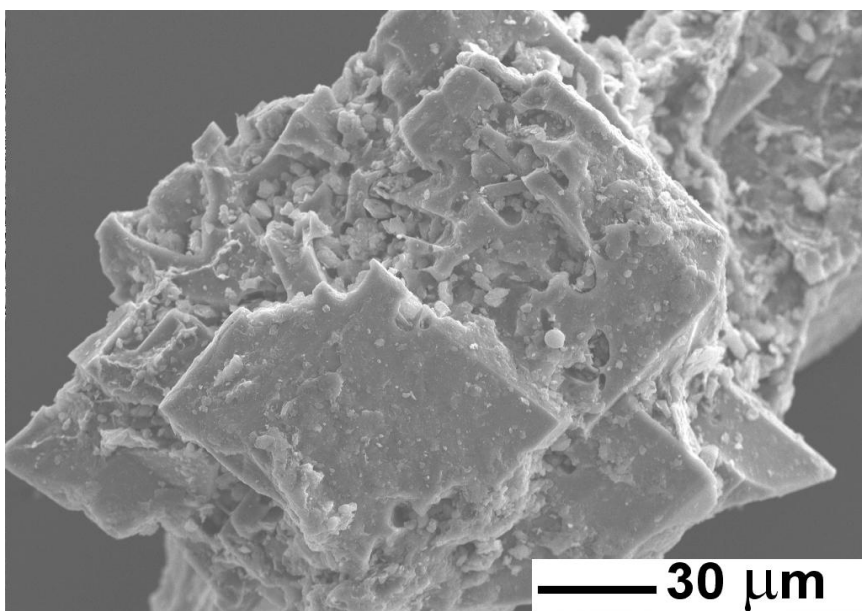


(h) FRP02 1029/116203: showing an agglomeration of fractured platy, tabular, cubic and prismatic crystals





(k) FRP02 1139/17463: an agglomeration of fractured cubic and tabular crystals with other debris



(l) FRP02 1145/17632: an agglomeration of fractured platy and tabular crystals

CHAPTER 5

Egyptian Blue Pellets from Piddington Roman Villa, Northampton

... by importing pigments ... this led to the arrival of specialized workers ...

Delamare & Guineau 1999, 33

5.1 Introduction

The Roman British Villa at Piddington (Map 3) is situated approximately six miles south-east of the City of Northampton. It was first discovered in the eighteenth century by workers quarrying limestone nearby. In the late 1980s a rescue dig began when a skeleton armed with a spear and a nearby gold ring were discovered. Also found in the same area were a mosaic and an underlying channelled hypocaust. A number of worked flints, such as blades, scrapers and arrow-heads were found during the exploration of the Roman villa area and surrounding fields indicating that the Piddington site had been occupied during the prehistoric period. Evidence from sherds of Claudian samian ware, amphorae and military equipment suggest that the Roman site may have been used as a military fort, constructed between AD 44 – 60, and occupied by the 14th Legion. The first proto-villa was built in about AD 65 and consisted of a rectangular wooden building with three rooms (Friendship-Taylor, 2006).

During the end of the first century, or early in the second century AD the first stone villa, a cottage-type villa, was developed. Later, towards the end of the second century it was expanded to become a wing-corridor-type villa having adjacent buildings on three sides. A bath-house was also completed during this period. At the end of the second century a fire destroyed most of the buildings

following which the occupants began to rebuild and refurnish the villa on a grand scale. However, at the end of the third century the continuing renovation of the villa appears to have come to a sudden end. The finding of an unworn coin dedicated to the emperor Allectus (AD 293-296) suggested to Friendship-Taylor (2006, 13:4) that the then occupiers who were ... *possibly supporters of Carausius / Allectus, started to rebuild the villa, only to have it confiscated on Allectus' defeat.* We know that ... *in times of civil war ... estates of the ... losing side were often confiscated by the state.* Figure 5.1 shows a drawing of how Piddington Roman Villa might have looked towards the end of the third century and figure 5.2 shows a sample of painted wall plaster from the villa, obtained from an in-fill during the 1999 excavation season.

The excavation of this site continues, under the direction of Roy and Elizabeth Friendship-Taylor and the Upper Nene Archaeological Society, where new and exciting discoveries are still being made. One such is evidence of 'squatters' moving into the abandoned ruins of the villa. These 'squatters' appear to have been industrious; a ceramic tile kiln, working surfaces and hearths have been found as well as large amounts of fourth century coins and Nene Valley fine-coated ware that date from the time of this occupation. It has been suggested that these so-called 'squatters' may have been the earliest inhabitants associated with what subsequently became the village of Piddington (Friendship-Taylor, 2006). Eleven Egyptian Blue pellets were found in two areas in the Roman Villa at Piddington. Pellet BM136 V/30 was found in a feature gully underlying the late first century villa; the remaining ten pellets were found in the midden area dating from the late third century. Figure 5.3 shows a plan of the site and the location where the pellets were found.

5.2 Analytical Investigations

Semi-quantitative geochemical techniques were employed in order to identify the elemental composition of these eleven pellets. The two main methods used to analyse these samples were Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) and Scanning Electron Microscopy - Energy Dispersive X-ray Analysis (SEM-EDAX).

Each of the pellets were weighed, measured and their colour identified using the Munsell Book of Color (Matt Finish Collection), second edition, 2001: the results are shown in figure 5.4. The described colours are subjective and should be considered as a guide only. The pellets were also examined under a MEIJI techno RZ zoom Stereomicroscope with a fibre-optic light source to study fine detail.

5.3 Results

The results of the **LA-ICP-MS** analysis show variations in the chemical elements found in the Egyptian Blue pellets of Piddington Roman Villa. Three of the pellets: ST116 FF/22, BM082 LL/24 and BM089 NN/29 contain both copper (Cu) and iron (Fe), whilst in BM070 MM/24, BM080 MM/29, BM054 TT/30, BM086 UU/22, BM127 VV/15, BM136 V/30 and West Field iron (Fe) is present but no copper is detected. However, in BM065 MM/25 copper is present but iron is not detectable.

Silica (Si) is present, in various amounts, in all the pellets with the exception of BM054 TT/30, BM086 UU/22, BM127 VV/15 and West Field. Lead (Pb) has been detected in all of the samples. Tin (Sn) has been identified in four of the pellets: ST116 FF/22, BM082 LL/24, BM089 NN/29, with a trace identified in West Field. Sodium (Na) has been detected in five of the pellets, namely: ST116 FF/22, BM065 MM/25, BM080 MM/29, BM089 NN/29 and also in

BM127VV/15 which may suggest that a sodium flux was used in the manufacture of these pellets. Calcium (Ca) is present in BM070 MM/24 and BM080 MM/29; traces of calcium have also been found in BM065 MM/25, BM086 UU/22 and BM127 VV/15. Both carbon (C) and lead (Pb) are present, in various quantities, in all the samples.

Barium (Ba) has been detected in five of the pellets: BM070 MM/24, BM080 MM/29, BM086 UU/22, BM127 VV/15 and West Field; traces of barium were also found in BM065 MM/25. Potassium (K) has been found in six of the pellets, namely: ST116 FF/22, BM080 MM/29, BM080 NN/29, BM054 TT/30, BM127 VV/15 and BM136 V/30. Traces of potassium were also been detected in BM086 UU/22 and in West Field. Differing amounts of Aluminium (Al) have been found in nine of the pellets: ST116 FF/22, BM082 LL/24, BM070 MM/24, BM080 MM/29, BM089 NN/29, BM054 TT/30, BM086 UU/22, BM136 V/30 and West Field. Magnesium (Mg) has been found in three of the pellets: BM080 MM/29, BM054 TT/30 and BM136 V/30. The elements, barium, potassium, aluminium and magnesium are commonly found the soil samples and were not unexpected finds given the differing amounts of soil with which the pellets were impregnated when they were examined.

The **SEM-EDAX** analysis showed that all the pellets contained large amounts of silica with various quantities of calcium, copper, iron, aluminium and carbon, although neither copper nor calcium were detected in the West Field pellet. In four of the pellets: BM070 MM/24, BM080 MM/29, BM089 NN/29 and BM086 UU/22 traces of sulphur (S) were identified. Evidence of sodium was found in five of the samples: BM082 LL/24, BM070 MM/24, BM065 MM/25, BM054 TT/30 and BM136 V/30. Only in the third of these five pellets is sodium also detected in the **LA-ICP-MS** analysis. Potassium has been

found in seven of the pellets: ST116 FF/22, BM082 LL/24, BM070 MM/24, BM065 MM/25, BM054 TT/30, BM136 V/30 and West Field. Traces of magnesium have been detected in six of the pellets: BM082 LL/24, BM070 MM/24, BM065 MM/25, BM054 TT/30, BM136 V/30 and West Field. Traces of titanium (Ti) were found in two of the samples: BM070 MM/24 and BM127 VV/15. Traces of chlorine (Cl) were indicated in BM070 MM/24. The finding of carbon, together with potassium in six pellets could be associated with a flux *ie* potash, that may have been used in the manufacture of these pellets. Tin, lead and barium are notably absent in all the samples.

The elemental composition of each of the eleven pellets studied with the LA-ICP-MS and SEM-EDAX analyses is shown in figure 5.5, and tabulated in figures 5.6A and 5.6B.

5.4 Texture and Structure of the Pellets

The texture and structure of all eleven pellets were examined under fibro-optic microscopy at a magnification of times 7.5 as shown in figure 5.7. Following experiments conducted by the author (see Chapter 9) it had been possible to detect, when looking microscopically at each pellet, the extent to which the ingredients had been ground and prepared prior to firing. Unlike the pellets at Fishbourne Roman Palace it has not been possible to categorize these Piddington pellets into different types. The ingredients of pellets ST116 FF/22, BM082 LL/24, and BM089 NN/29 have been roughly ground; the quartz grains are large and there are some inclusions. In BM070 MM/24, BM065 MM/25, BM080 MM/29 and BM136 V/30, by contrast, the ingredients have been finely ground; no inclusions or large grains of quartz could be seen. When the microscopic picture of the West Field pellet is examined it can be seen that this pellet looks very different from the other ten: whereas in all the other pellets

individual grains of different sizes can be identified, in the West Field pellet the grains appear to have fused into a more-or-less continuous sheet looking like bubbling lava flow, being somewhat botryoidal in appearance.

With detailed examination of the pellets under high power microscopy the grains sizes were seen to vary considerably. Figure 5.8a, pellet ST116 FF/22, shows grains that give the appearance of being unwashed, indicated by the red arrows: the blue arrows shows the presence of much small quartz grains. Figure 5.8b, pellet BM080 MM/29 again shows the small size of the quartz grains when compared to the size of the unwashed grains. The different size grains found in pellet BM082 LL/24 are shown in figure 5.8c. As in the previous figure a small grain of quartz is identified by a blue arrow. The green arrow shows a single well defined washed grain amongst several unwashed grains, shown by the red arrows.

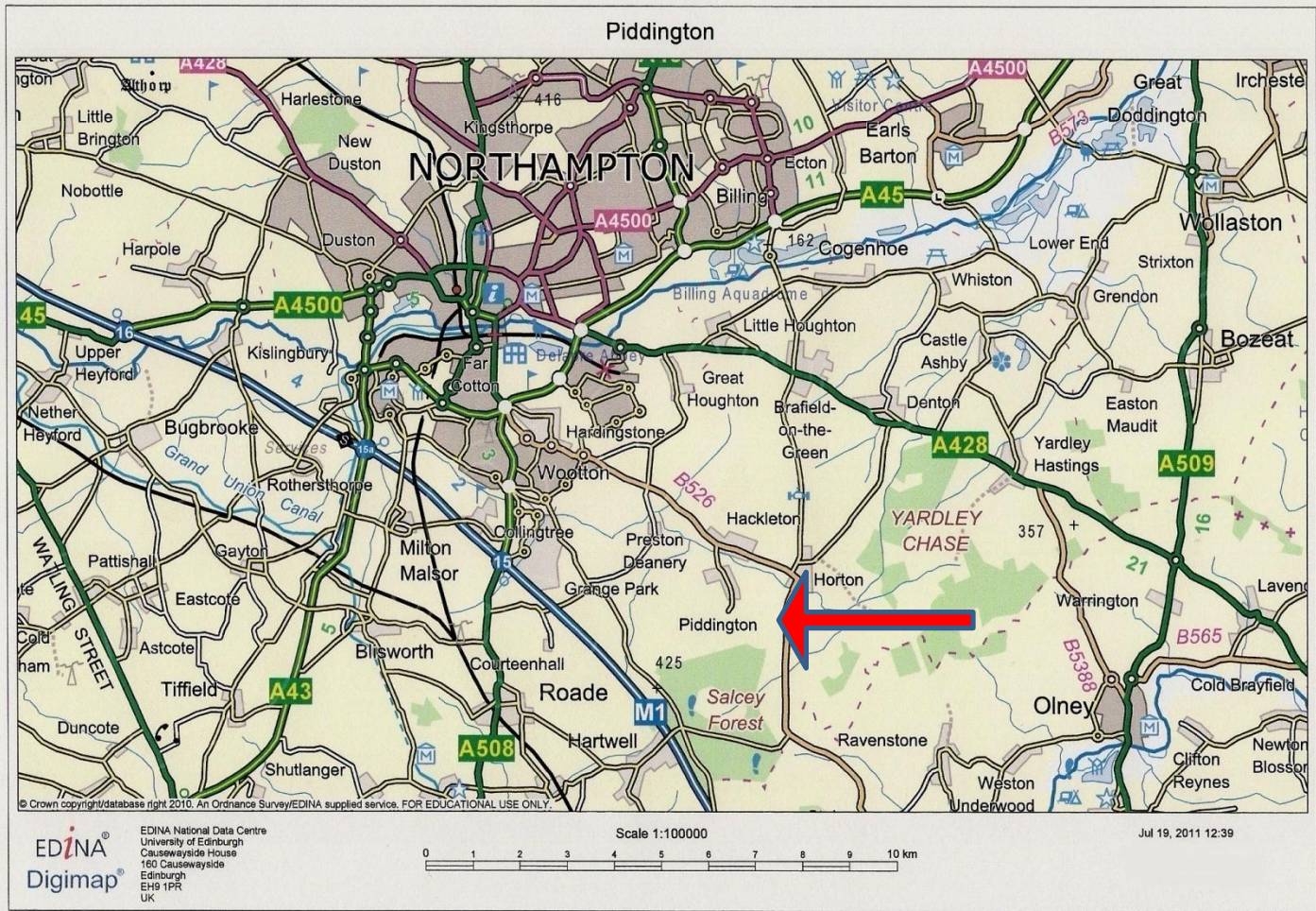
5.5 Discussion

The results of the LA-ICP-MS suggest that the majority of Piddington's pellets, containing carbon, and lead. Tin was found in four pellets, *viz.* ST116 FF/22, BM080 MM/29, BM089 NN/29 and West Field; these four pellets also contained carbon and lead and other components such as copper and iron which may suggest that these Egyptian Blue pellets may have been manufactured from scraps of metal discarded by the Villa's workshops. To date, no archaeological evidence has been found to suggest that any of the Piddington pellets were manufactured at a 'factory site' within the vicinity of the Roman Villa.

The results of the SEM-EDAX analysis shows a similar elemental composition for the following three pellets: ST116 FF/22, BM080 MM/29 and BM089 NN/29. This may suggest that these pellets had been produced using Vitruvius'

recommended ingredients (Book VII, 219,1) although in the LA-ICP-MS data there is a high tin content both in ST116 FF/22 and BM089 NN/29 and but none in BM080 MM/29. Lead is present in differing quantities in all three pellets. It could be suggested, therefore, that these three pellets may have been contaminated in the manufacturing process.

The apparent uniform texture, structure and fabric of the pellets can be seen in figure 5.4. Similarly, the SEM-EDAX details of the crystal structure (which show uniformly amorphous habits with few identifiable tabular, platy and cubic crystal faces) would suggest that all the pellets came from a similar 'manufacturing process'. However, it has been established that pellet BM136 V/30 is from a first century AD strata whereas the other 10 pellets were found in a maiden area dating to the third century. Of the later, the West Field pellet shows some distinct characteristics: microscopically it shows no individual grains but gives the appearance of a single, fused, botryoidal sheet. Additionally, the analyses might suggest that its chemistry is distinct: neither the LA-ICP-MS nor the SEM analyses have identified the presence of copper or calcium; silica is only identified by SEM-EDAX. Thus although the 10 pellets have a similar date, it would appear that that found in the West Field, at least, should be regarded as being from a distinct batch.



Map 3. Showing location of Piddington Roman Villa

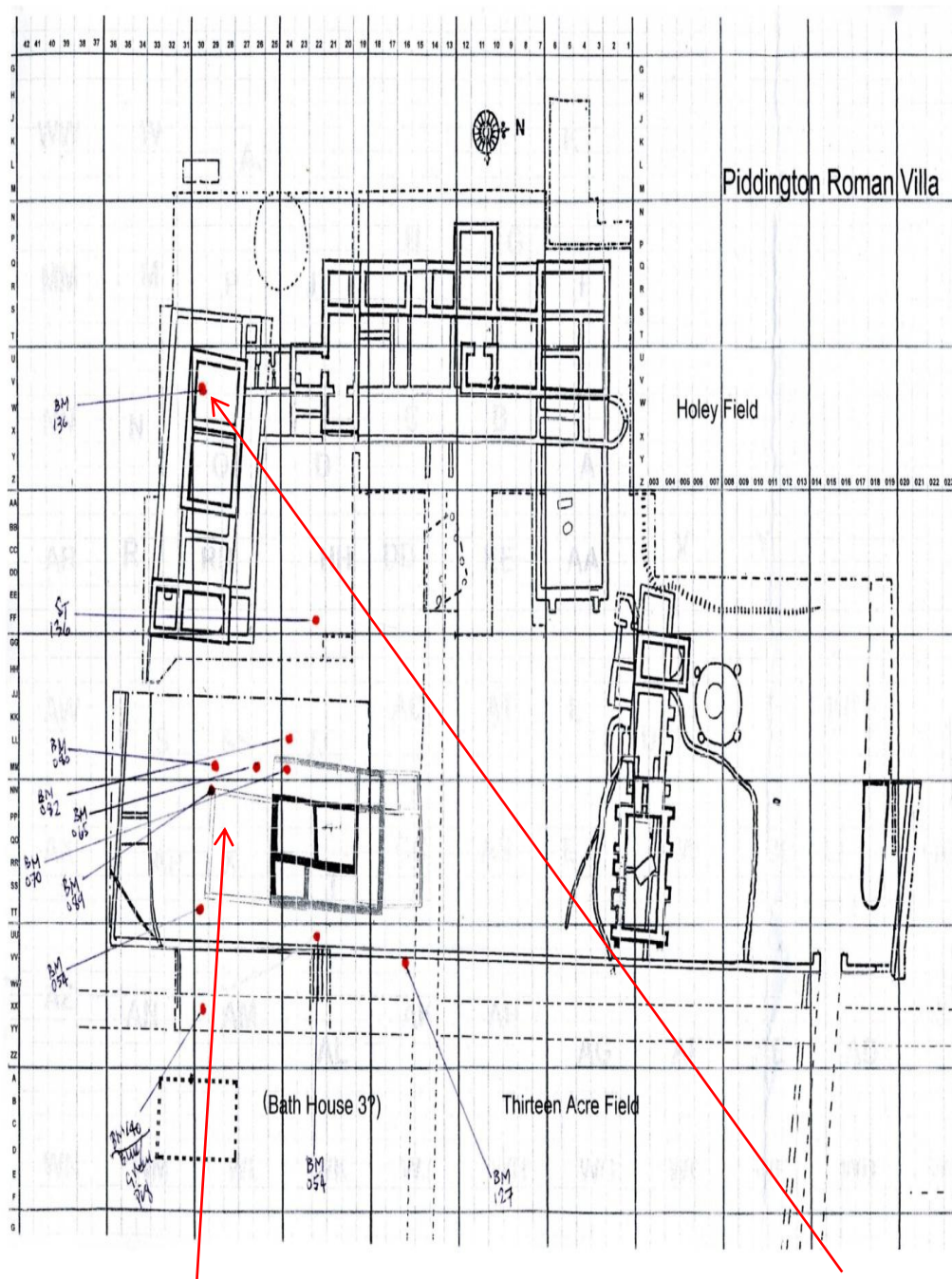
Figure 5.1 Tiberius Claudius Severus and his family outside Piddington Roman Villa (Drawing of Piddington Roman Villa)



Figure 5.2 Painted Plaster Piddington Roman Villa
Picture taken by author.

By kind permission of R M & D E Friendship-Taylor

Figure 5.3 Site Plan of Piddington Roman Villa



Shows where the majority of the pellets were found in a Roman midden dating from the late 3rd Century AD.

BM136 V/30 was found in a feature gully, underlying the late 1st Century Villa

Figure 5.4 Showing weight, dimensions and colour of Piddington Roman Villa's pellets



(a) ST116FF/22

Weight: 2.04g

Dimensions: 15.58 x 13.47 mm

Munsell No. 5PB 5/10



(b) BM082 LL/24

Weight: 0.54g

Dimensions: 9.46 x 8.68 mm

Munsell No. 5PB 4/8



(c) BM070 MM/24

Weight: 1.09g

Dimensions: 17.26 x 15.45

Munsell No. 5PB 6/8



(d) BM065 MM/25

Weight: 0.15g

Dimensions: 9.12 x 4.76

Munsell No. 5PB 6/8



(e) BM080 MM/29

Weight: 0.36g

Dimensions: 9.34 x 8.66 mm

Munsell No. 5PB 5/8



(f) BM089 NN/29

Weight: 2.24g

Dimensions: 21.27x 14.04 mm

Munsell No. 5PB 5/10



(g) BM054 TT/30

Weight: 0.48g

Dimensions: 8.12 x 7.82 mm

Munsell No. 5PB 7/6



(h) BM086 UU/22

Weight: 1.11g

Dimensions: 14.55 x 10.91 mm

Munsell No. 5PB 6/8



(i) BM127 VV/15

Weight: 2.29g

Dimensions: 15.44 x 15.26 mm

Munsell No. 5PB 5/10



(j) BM 136 V/30
Weight: 1.88
Dimensions: 14.56 x 13.33mm

Munsell No. 5PB 7/6



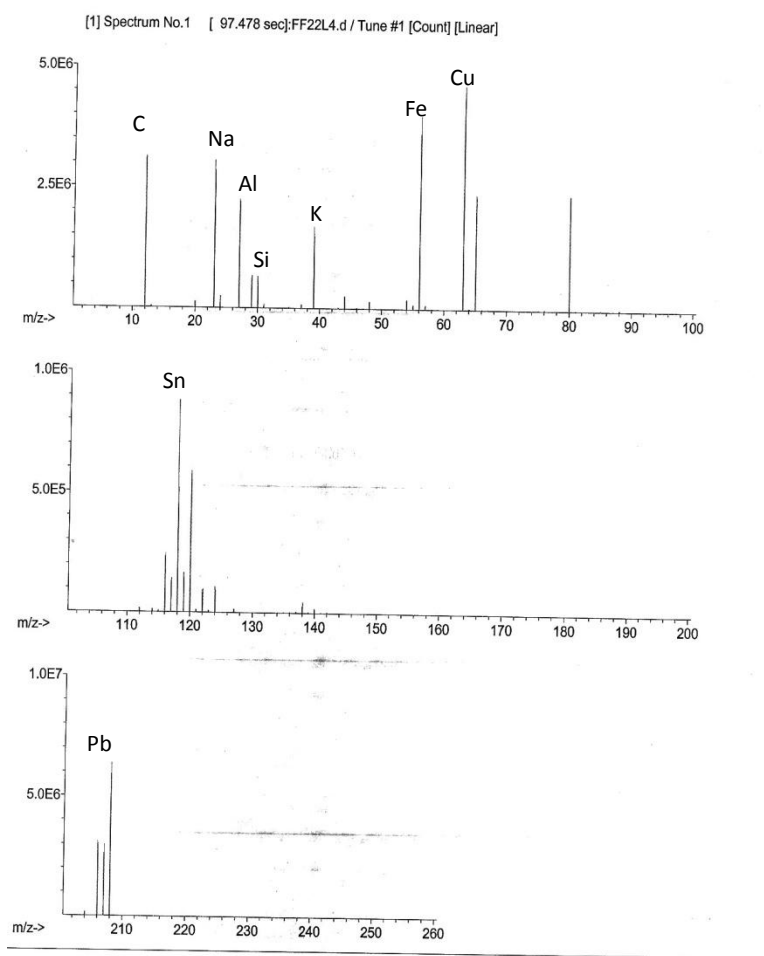
(k) West Field

Weight: 2.76g
Dimensions: 16.92 x 15.35 mm

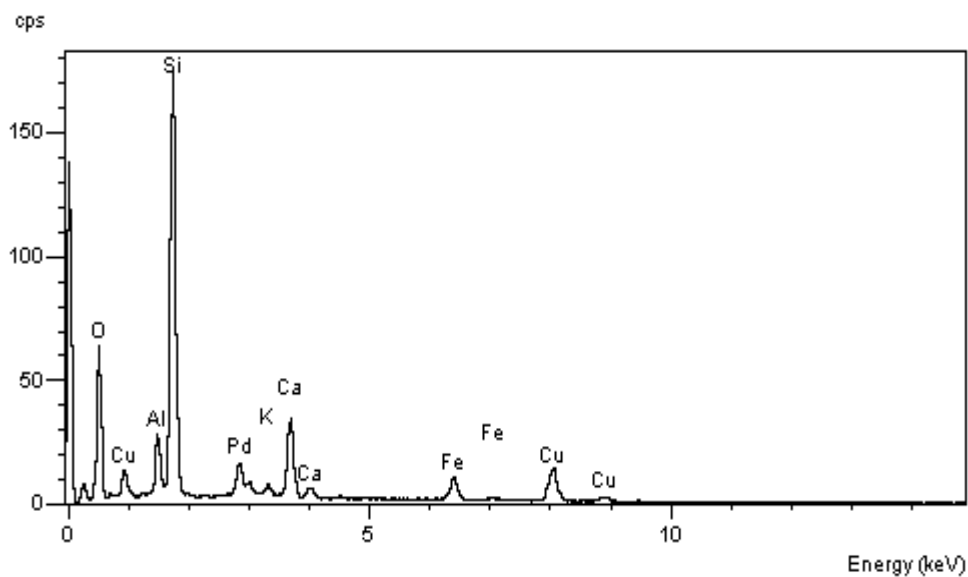
Munsell No. 5PB 6/8

Figure 5.5 LA-ICP-MS and SEM-EDAX results for Piddington Roman Villa

(a) ST116 FF/22

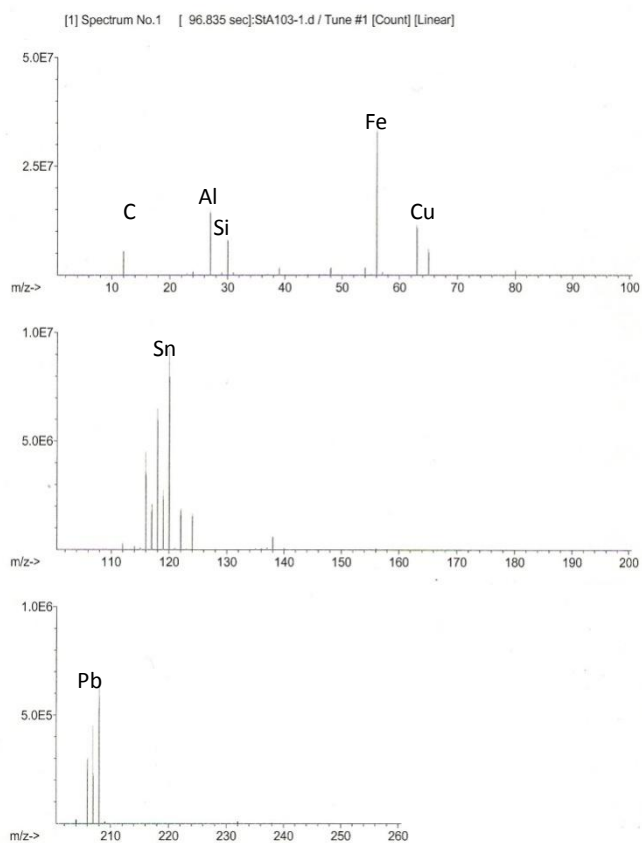


EDX energy spectrum for LA-ICP-MS

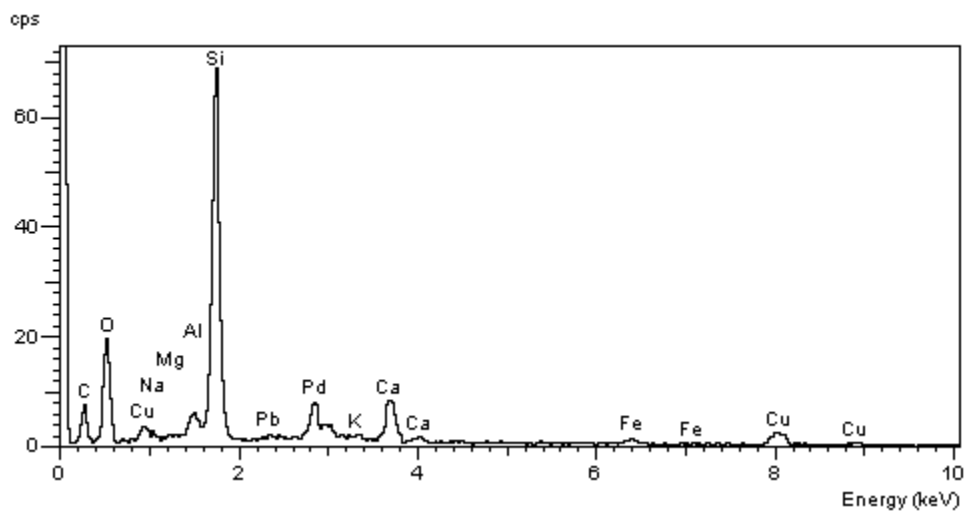


EDX energy spectrum for SEM-EDAX

(b) BM082 LL/24

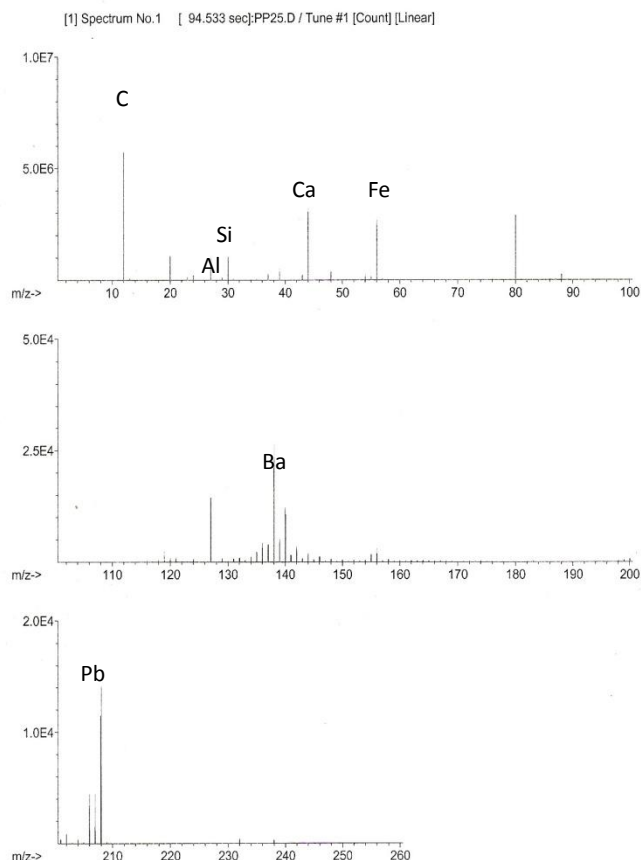


EDX energy spectrum for LA-ICP-MS

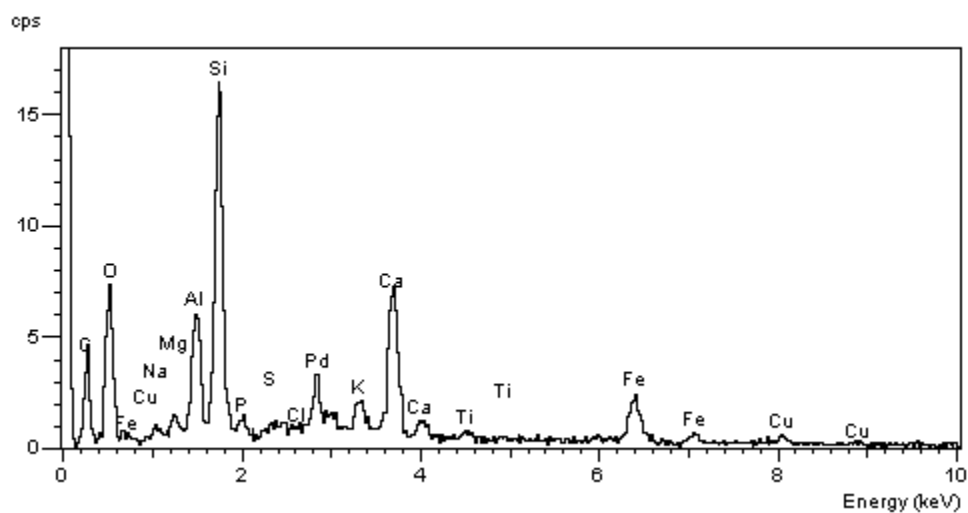


EDX energy spectrum for SEM-EDAX

(c) BM070 MM/24

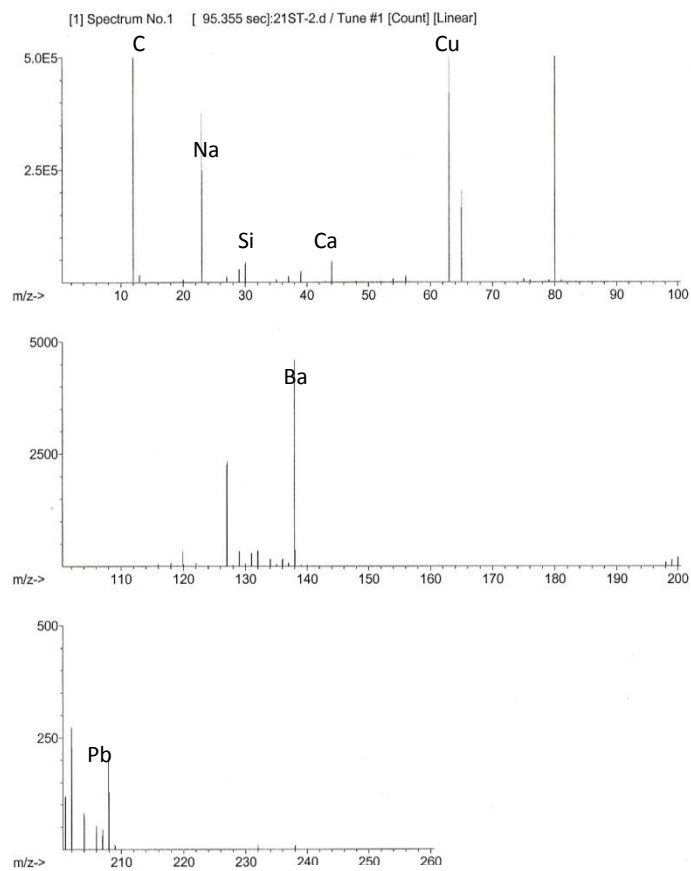


EDX energy spectrum for LA-ICP-MS

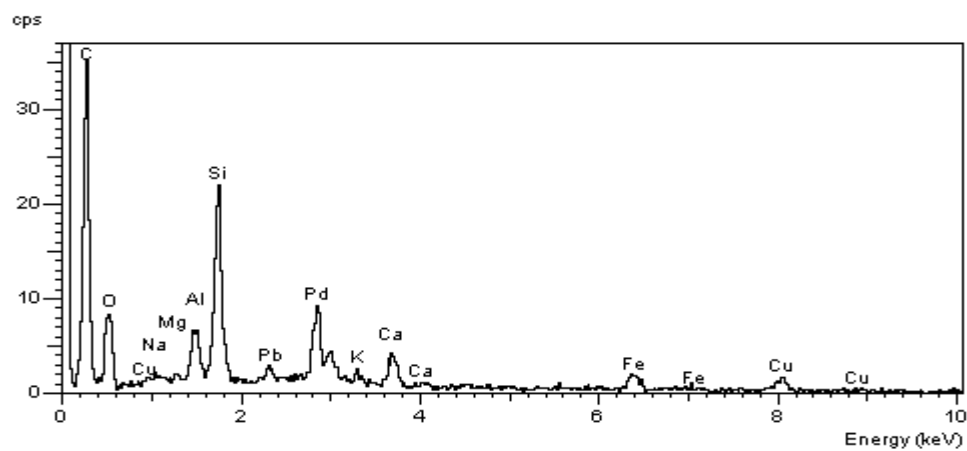


EDX energy spectrum for SEM-EDAX

(d) BM065 MM/25

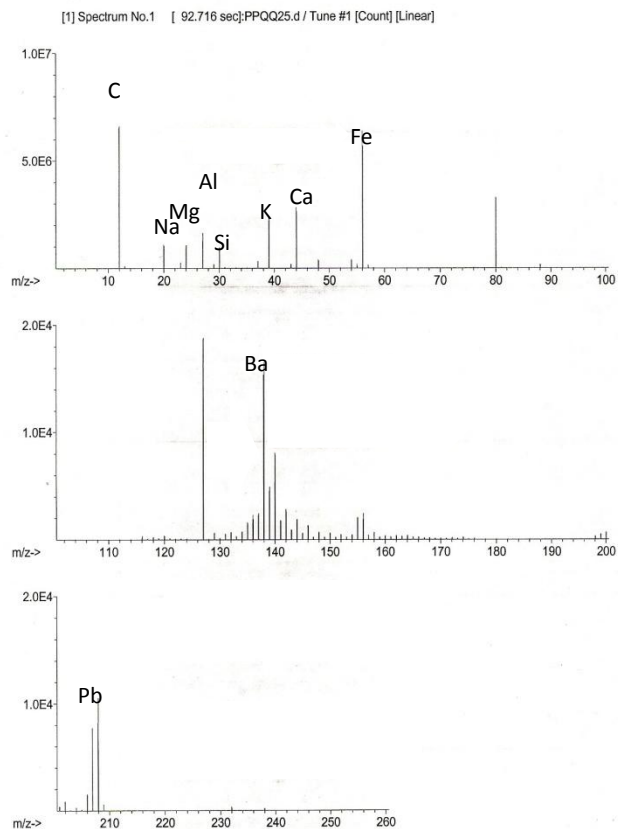


EDX energy spectrum for LA-ICP-MS

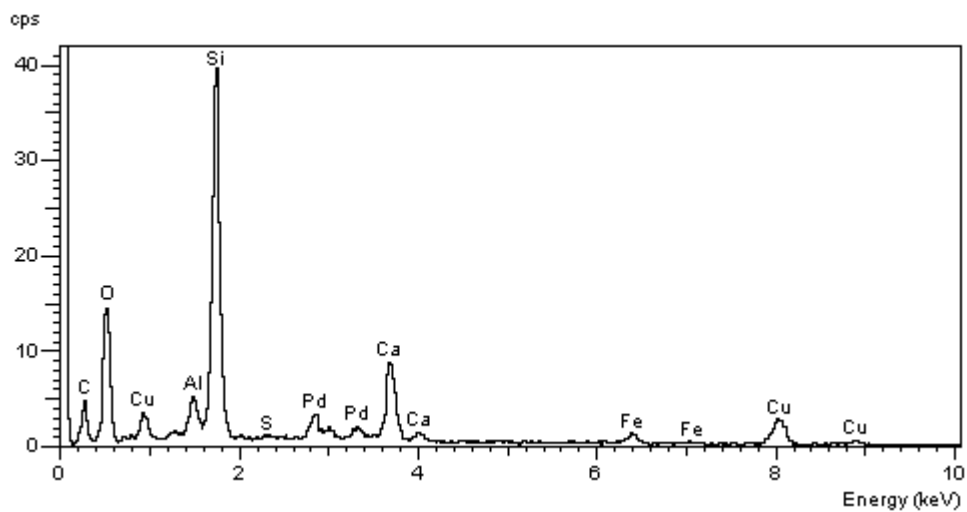


EDX energy spectrum for SEM-EDAX

(e) BM080 MM/29

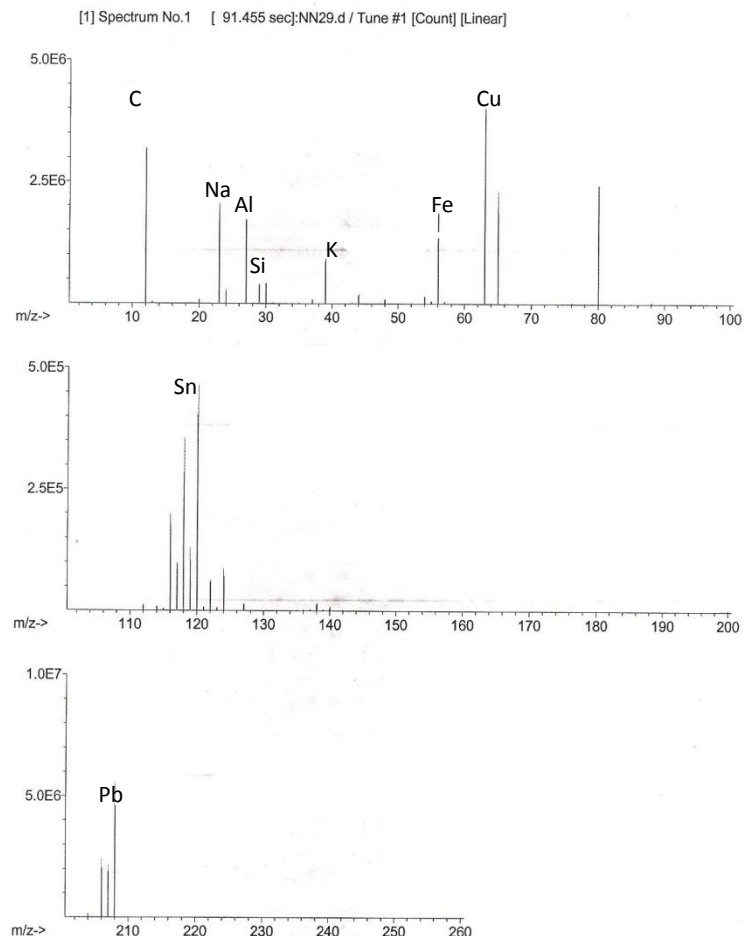


EDX energy spectrum for LA-ICP-MS

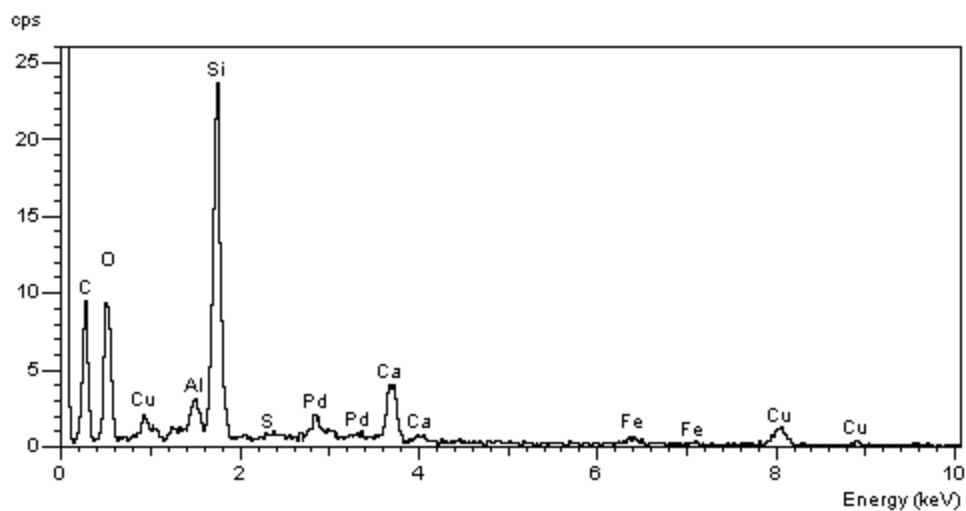


EDX energy spectrum for SEM-EDAX

(f) BM089 NN/29

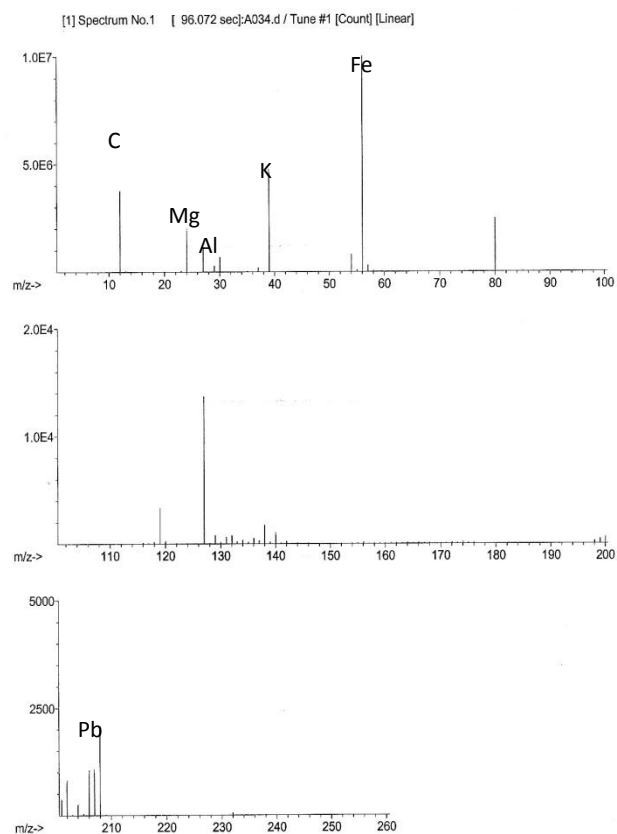


EDX energy spectrum for LA-ICP-MS

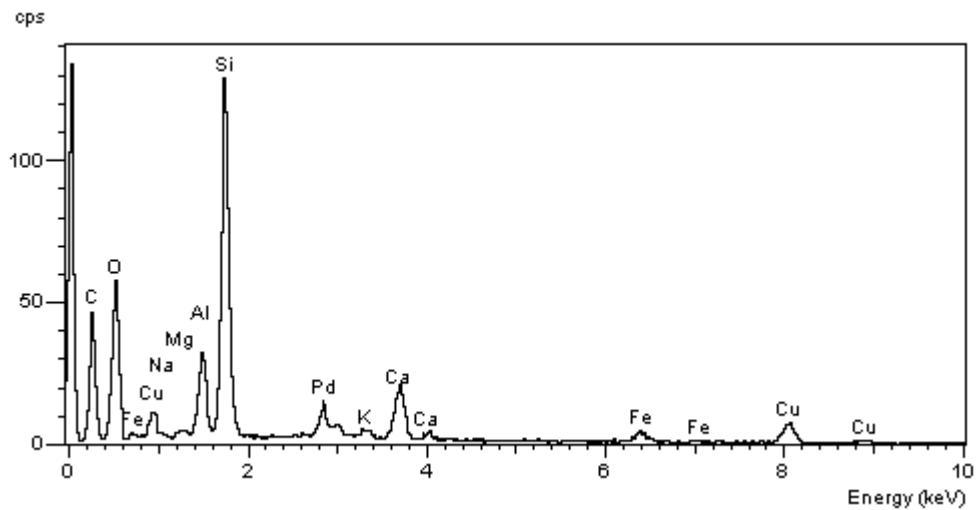


EDX energy spectrum for SEM-DAX

(g) BM054 TT/30

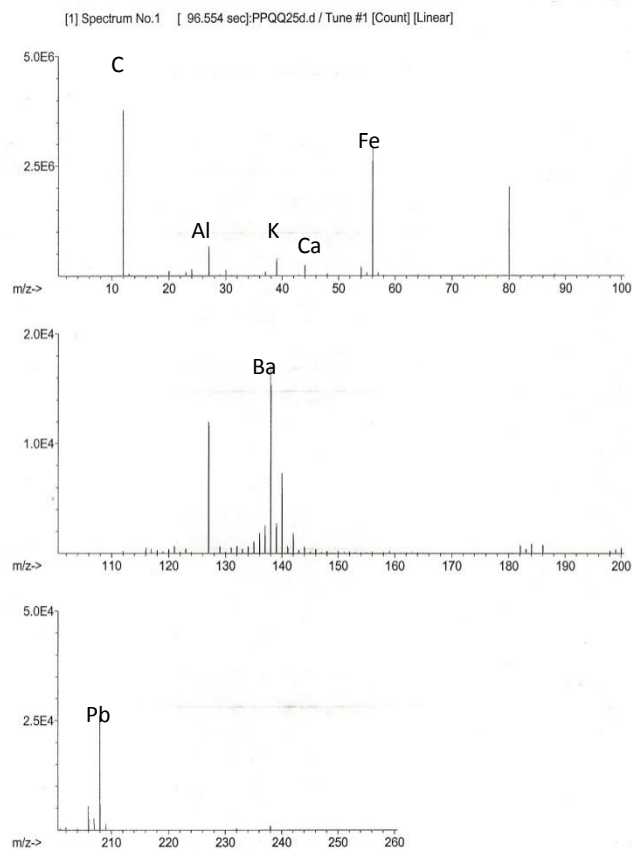


EDX energy spectrum for LA-ICP-MS

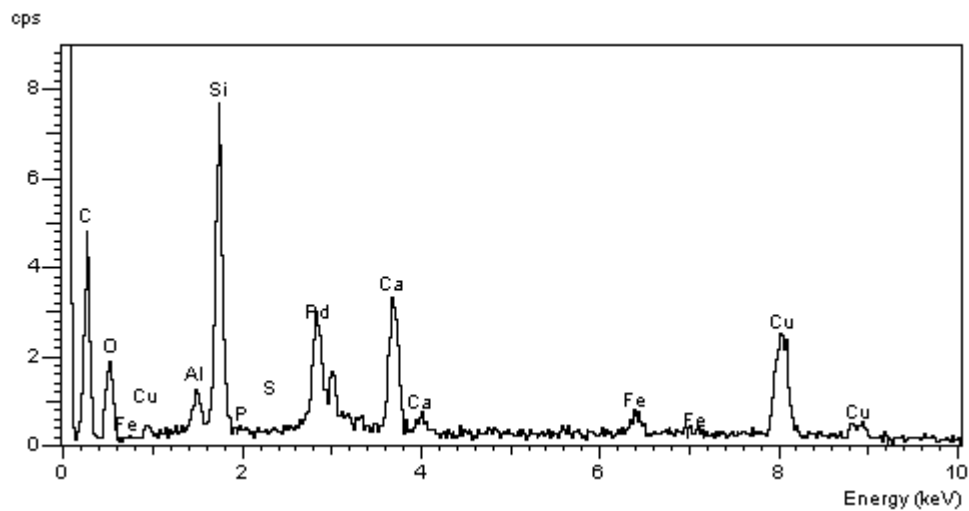


EDX energy spectrum for SEM-EDAX

(h) BM086 UU/22

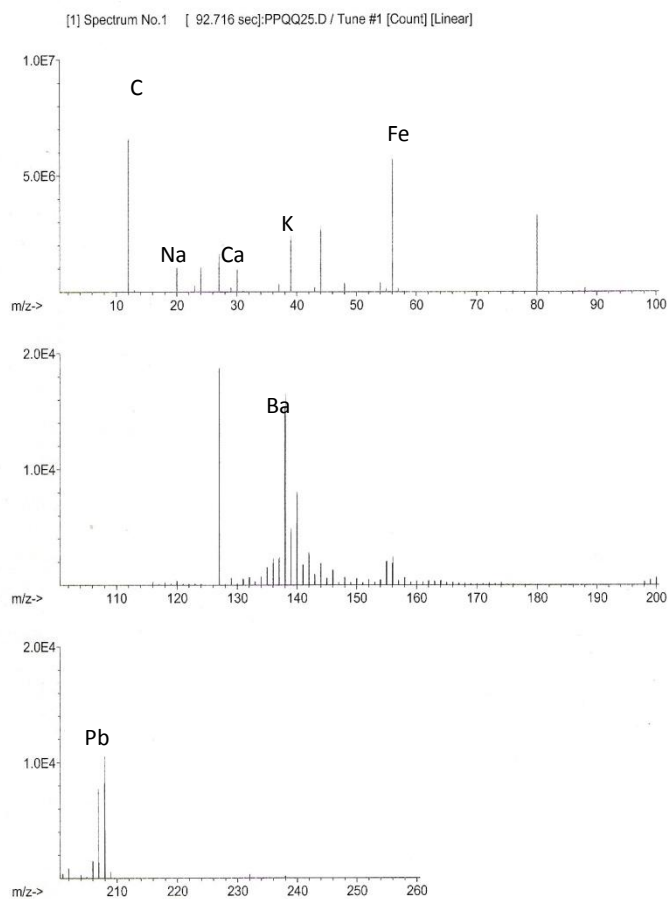


EDX energy spectrum for LA-ICP-MS

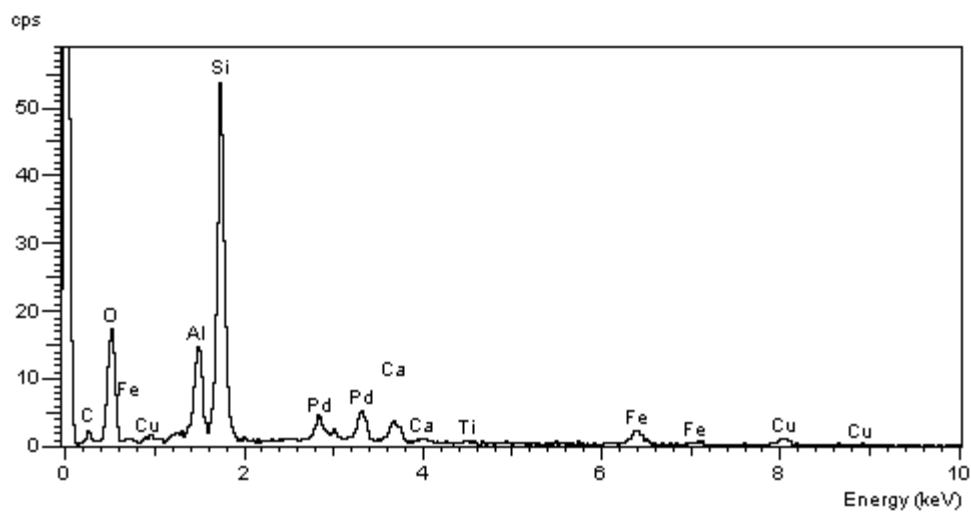


EDX energy spectrum for SEM-EDAX

(i) BM127 VV/15

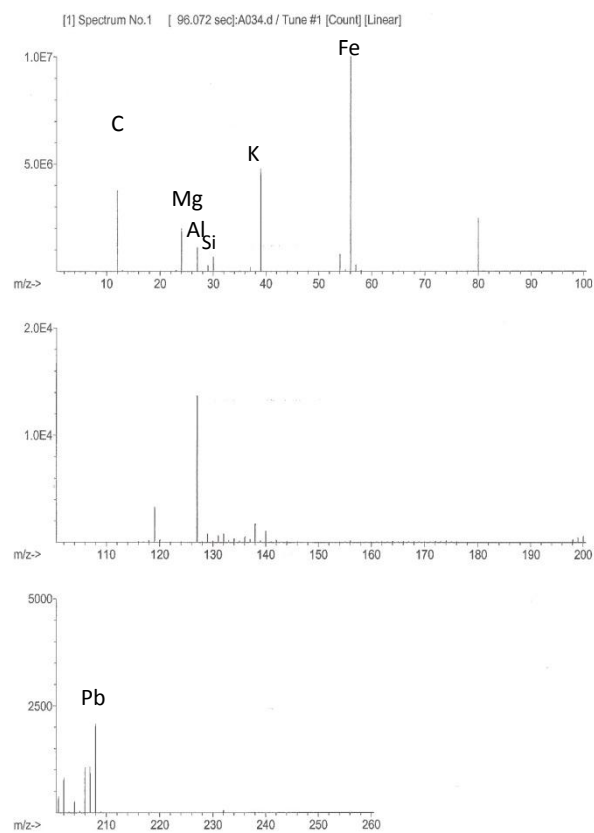


EDX energy spectrum for LA-ICP-MS

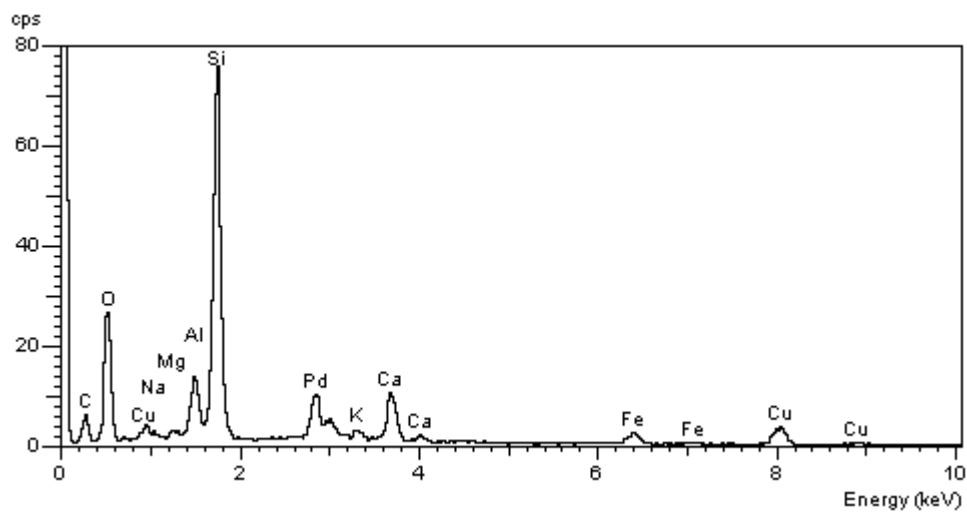


EDX energy spectrum for SEM-EDAX

(j) BM136 V/30

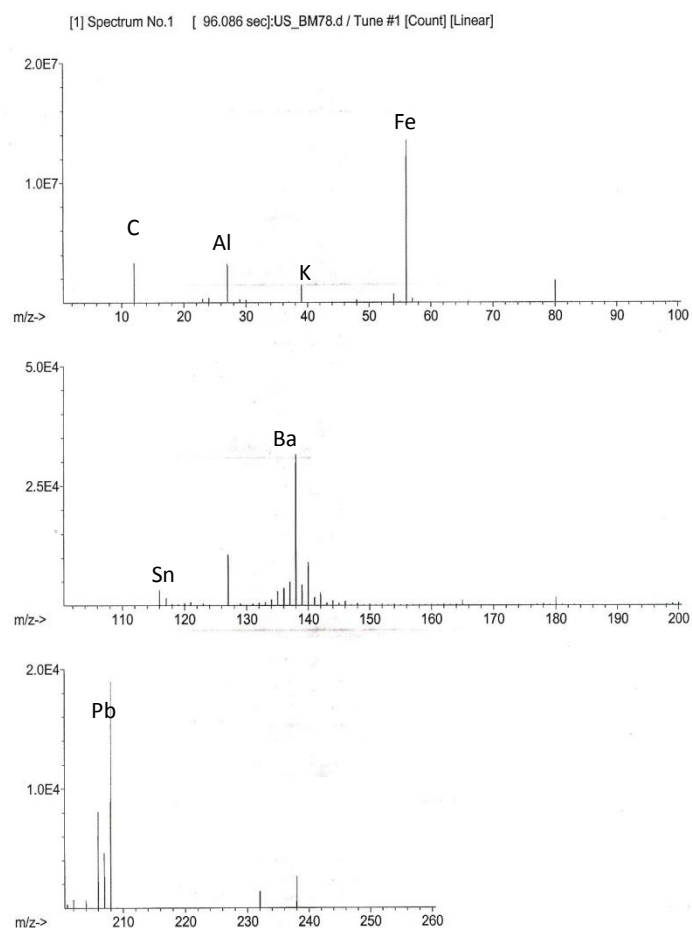


EDX energy spectra for LA-ICP -MS

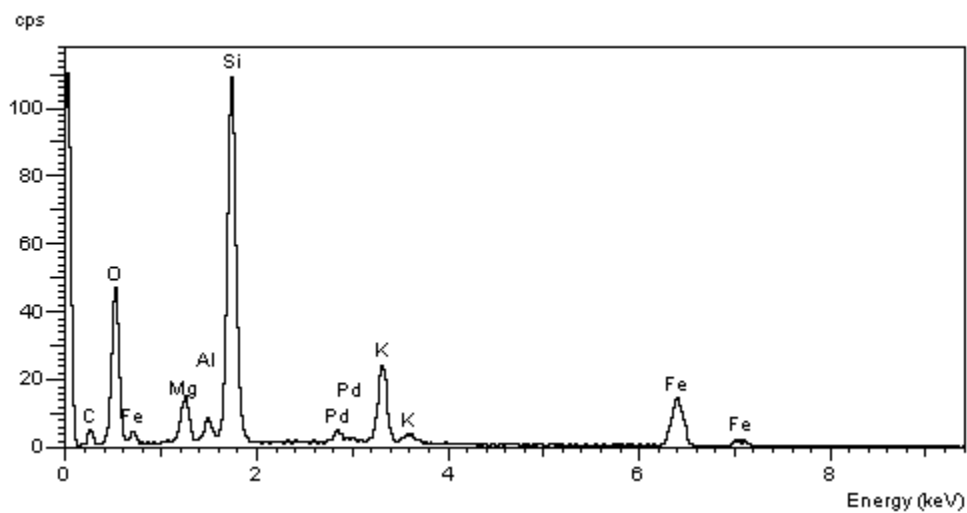


EDX energy spectra for SEM-EDAX

(k) West Field



EDX energy spectrum for LA-ICP-MS



EDX energy spectrum for SEM-EDAX

Figure 5.6A

**Summary of elements detected by LA-ICP-MS Analysis
of Egyptian Blue pellets found at Piddington Roman Villa**

| | C | Cu | Fe | Si | Pb | Sn | Na | Ca | Ba | K | Al | Mg |
|-------------|---|----|----|----|----|----|----|----|----|---|----|----|
| ST116 FF/22 | x | x | x | x | x | x | x | | | x | x | |
| BM082 LL/24 | x | x | x | x | x | x | | | | | x | |
| BM070 MM/24 | x | | x | x | x | | | x | x | | x | |
| BM065 MM/25 | x | x | | x | x | | x | x | x | | | |
| BM080 MM/29 | x | | x | x | x | | x | x | x | x | x | x |
| BM089 NN/29 | x | x | x | x | x | x | x | | | x | x | |
| BM054 TT/30 | x | | x | | x | | | | | x | x | x |
| BM086 UU/22 | x | | x | | x | | | x | x | x | x | |
| BM127 VV/15 | x | | x | | x | | x | x | x | x | | |
| BM136 V/30 | x | | x | x | x | | | | | x | x | x |
| West Field | x | | x | | x | x | | | x | x | x | |

| | | | | |
|--------------|----|---------|----|-----------|
| KEY : | C | Carbon | Na | Sodium |
| | Cu | Copper | Ca | Calcium |
| | Fe | Iron | Ba | Barium |
| | Si | Silicon | K | Potassium |
| | Pb | Lead | Al | Aluminium |
| | Sn | Tin | Mg | Magnesium |

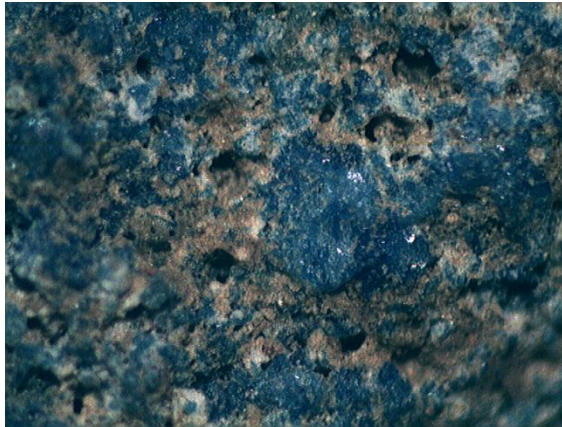
Figure 5.6B

Summary of elements detected by SEM-EDAX analysis of the Egyptian Blue pellets found at Piddington Roman Villa

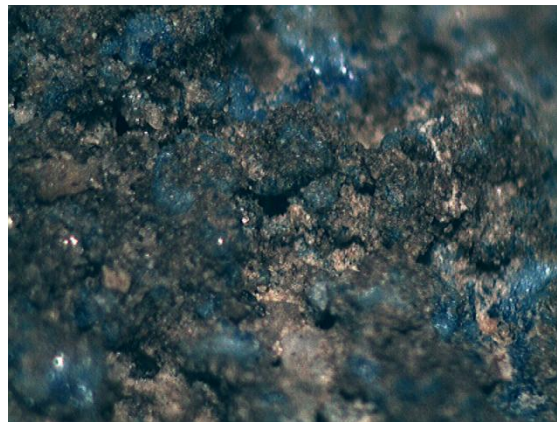
| | C | Cu | Fe | Si | Pb | Sn | Na | Ca | Ba | K | Al | Mg | Ti | S | P |
|-------------|---|----|----|----|----|----|----|----|----|---|----|----|----|---|---|
| ST116 FF/22 | | x | x | x | | | | x | | x | x | | | | |
| BM082 LL/24 | x | x | x | x | x | | x | x | | x | x | x | | | |
| BM070 MM/24 | x | x | x | x | | | x | x | | x | x | x | x | x | x |
| BM065 MM/25 | x | x | x | x | x | | x | x | | x | x | x | | | |
| BM080 MM/29 | x | x | x | x | | | | x | | | x | | | x | |
| BM089 NN/29 | x | x | x | x | | | | x | | | x | | | x | |
| BM054 TT/30 | x | x | x | x | | | x | x | | x | x | x | | | |
| BM086 UU/22 | x | x | x | x | | | | x | | | x | | | | |
| BM127 VV/15 | x | x | x | x | | | | x | | | x | | x | x | |
| BM136 V/30 | x | x | x | x | | | x | x | | x | x | x | | | |
| West Field | x | | x | x | | | | | | x | x | x | | | |

| | | | | |
|--------------|----|---------|----|------------|
| KEY : | C | Carbon | Ca | Calcium |
| | Cu | Copper | Ba | Barium |
| | Fe | Iron | K | Potassium |
| | Si | Silicon | Al | Aluminium |
| | Pb | Lead | Mg | Magnesium |
| | Sn | Tin | Ti | Titanium |
| | Na | Sodium | S | Sulphur |
| | | | P | Phosphorus |

Figure 5.7 Piddington Roman Villa Pellets at
Magnification of x 7.5



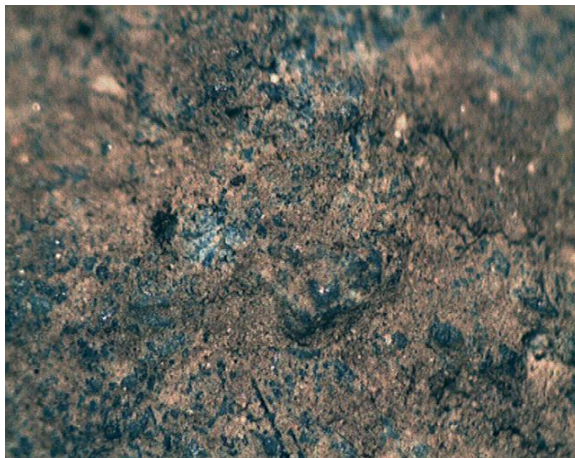
(a) ST116 FF/22



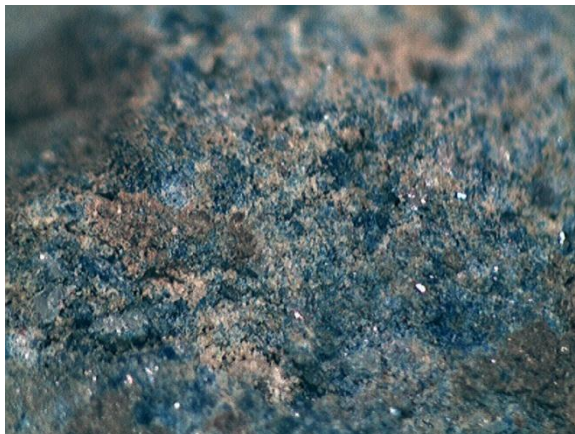
(b) BM082 LL/24



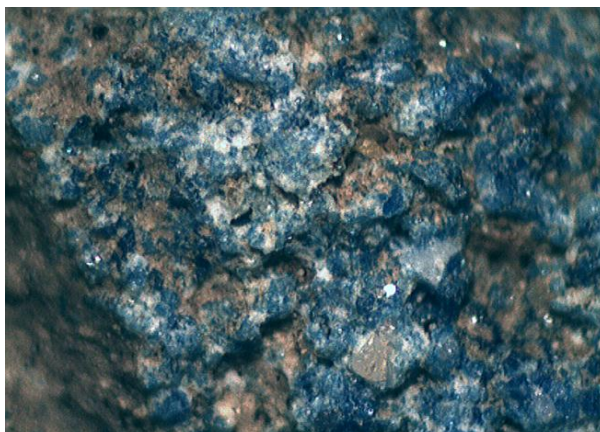
(c) BM070 MM/24



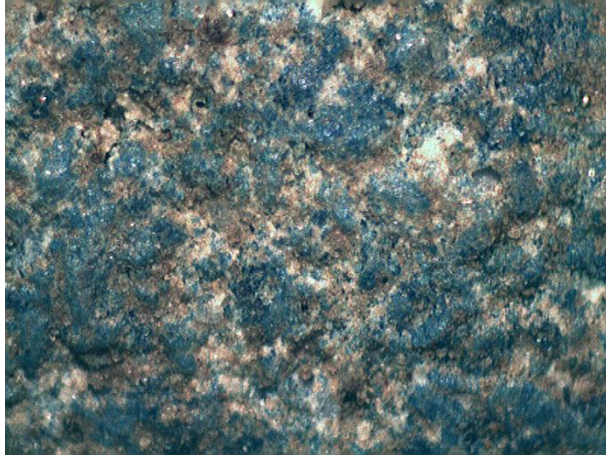
(d) BM065 MM/25



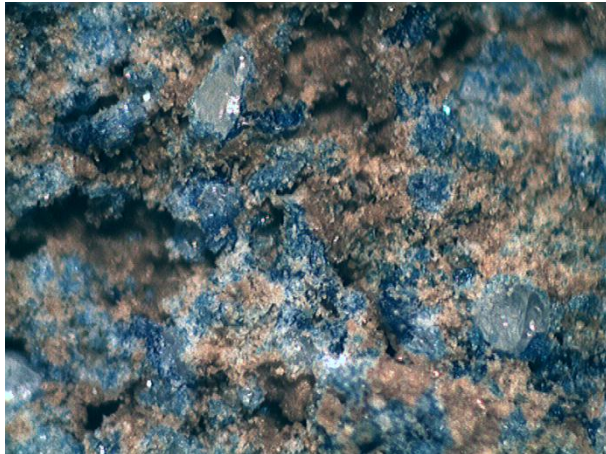
(e) BM080 MM/29



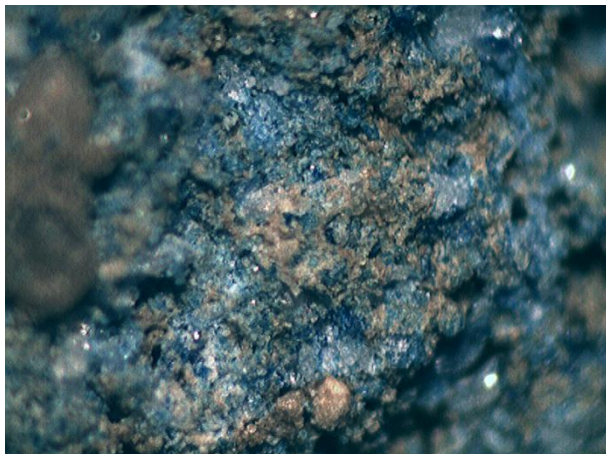
(f) BM089 NN/29



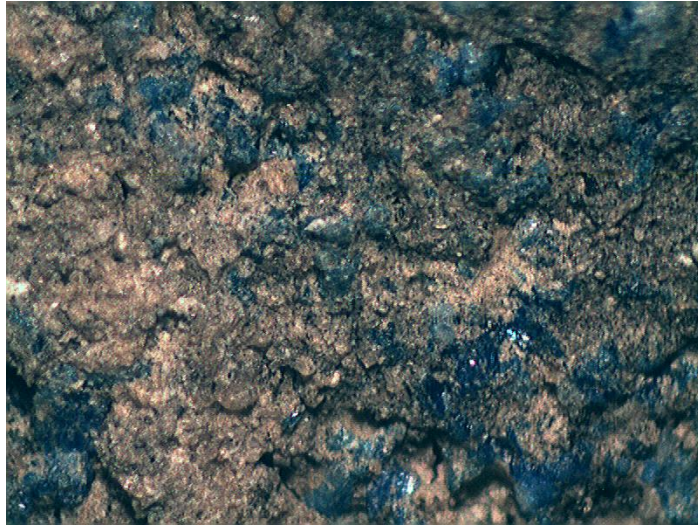
(g) BM054 TT/30



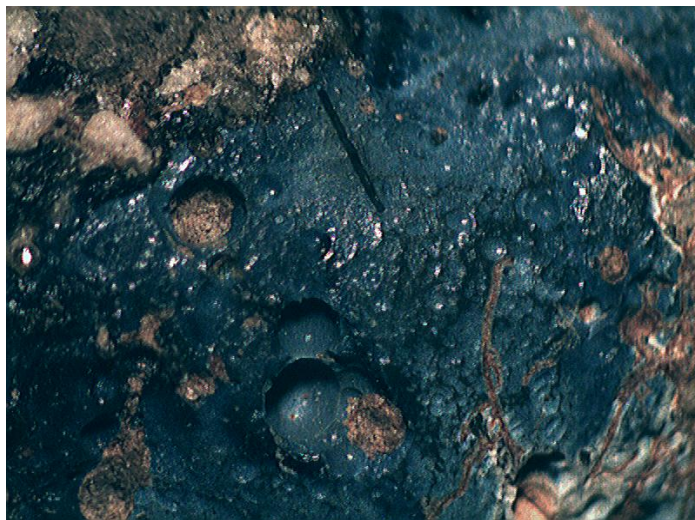
(h) BM086 UU/22



(i) BM127 VV/15

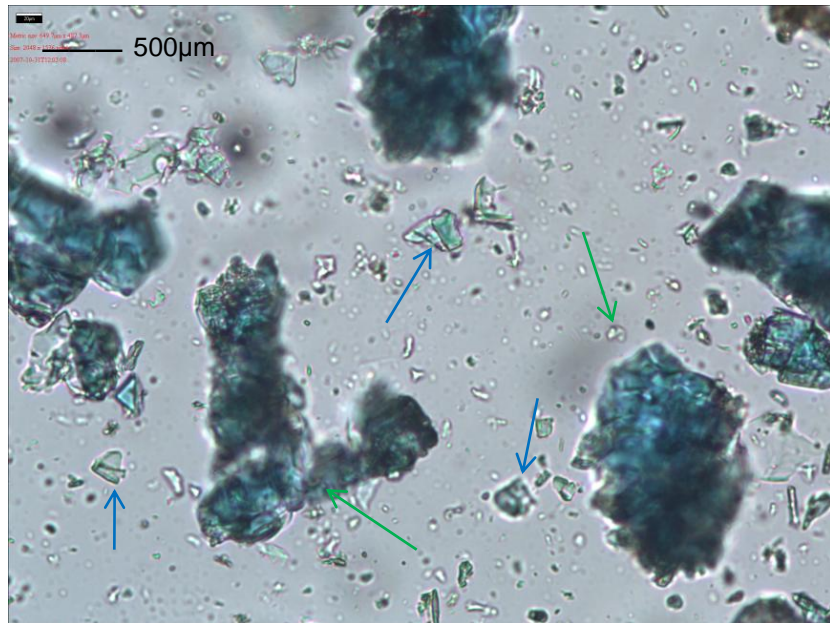


(j) BM136 V/30

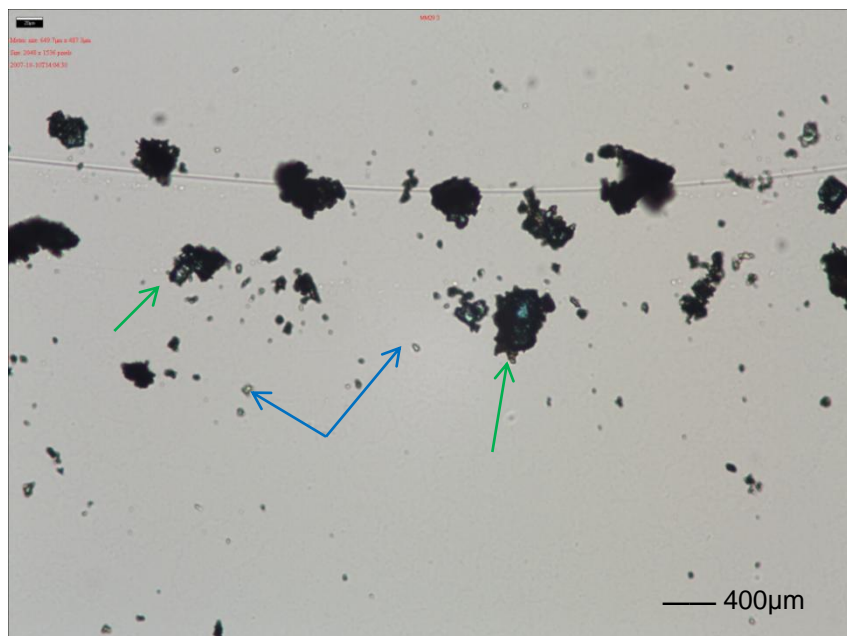


(k) West Field.

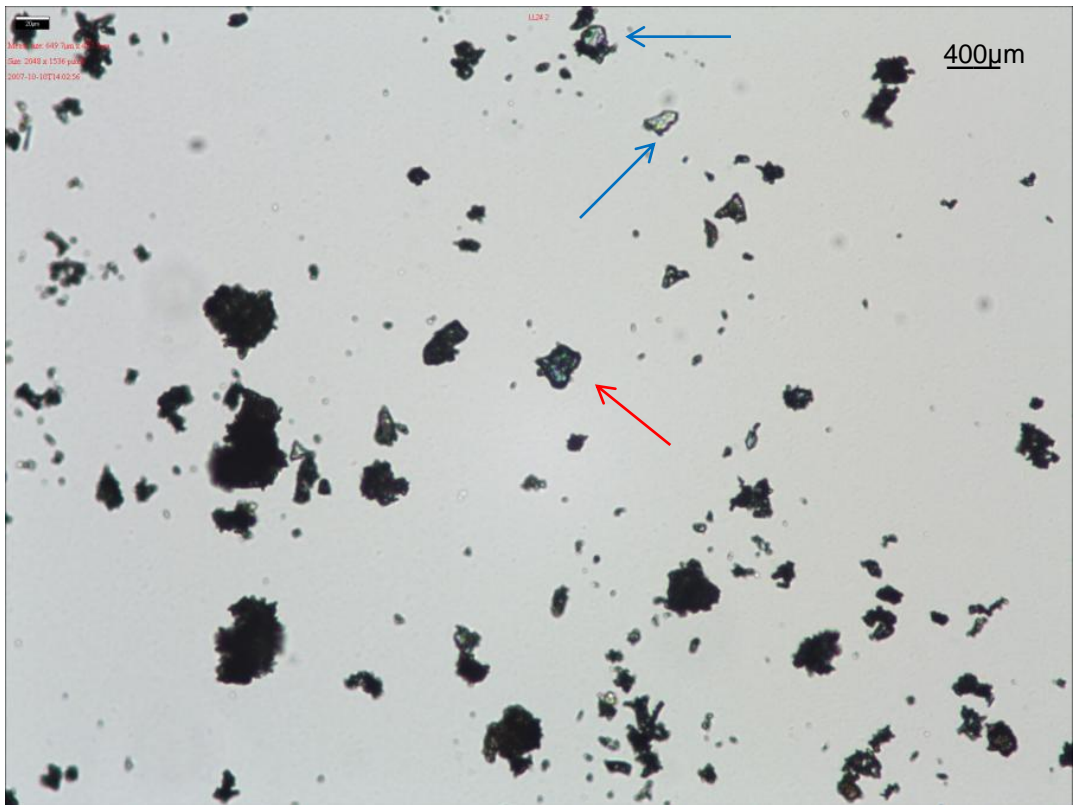
Figure 5.8 An example of the grain structure and size of the pellets from Piddington Roman Villa



(a) ST116 FF/22. The green arrows show clearly show unwashed grains whilst the blue arrows small grains of quartz

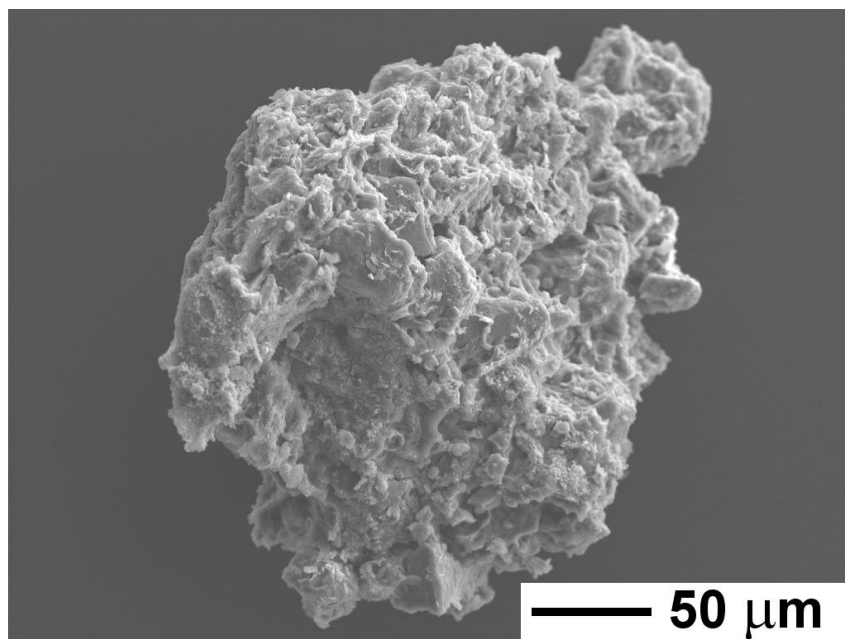


(b) BM080 MM/29. Unwashed grain is highlighted by green arrow. Small quartz grains by blue arrows

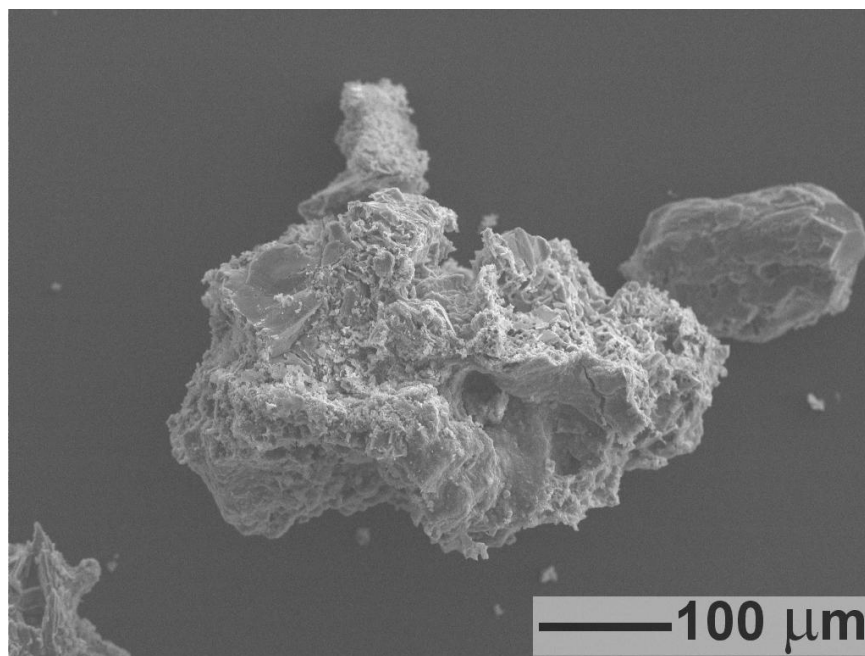


(c) BM082 LL/24. Blue arrows points to small quartz grains. The red arrow shows a washed grain

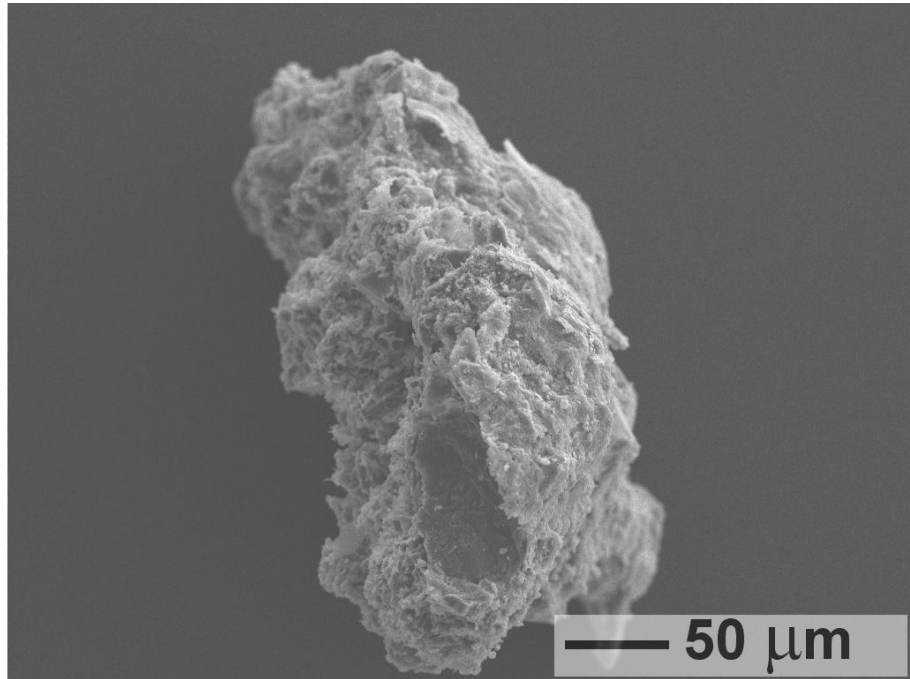
Figure 5.9 Showing the crystal habit of Piddington pellets



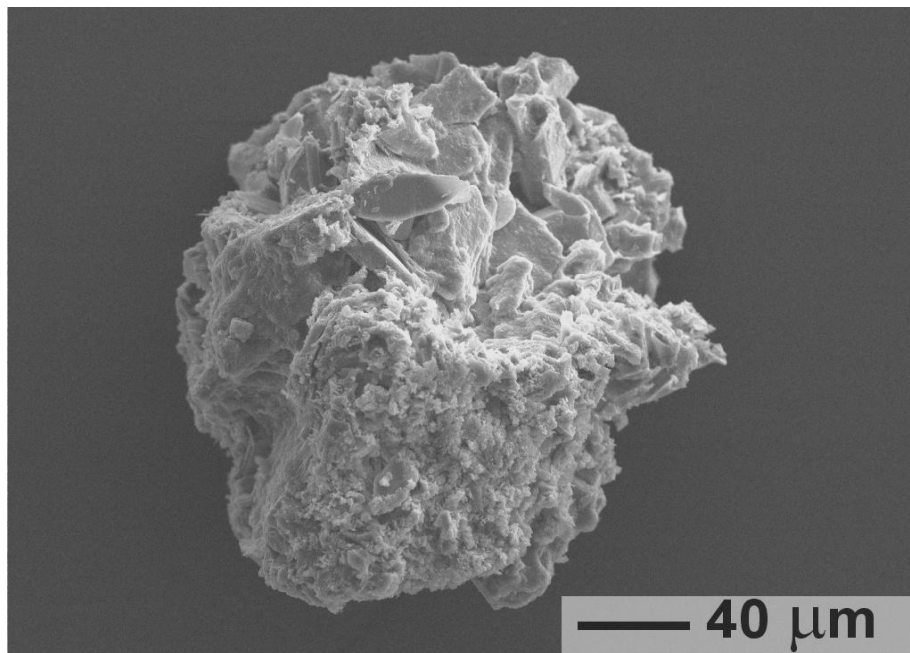
(a) ST116 FF/22: an amorphous agglomeration in which only a few fragments of cubic, platy and tabular crystals can be identified



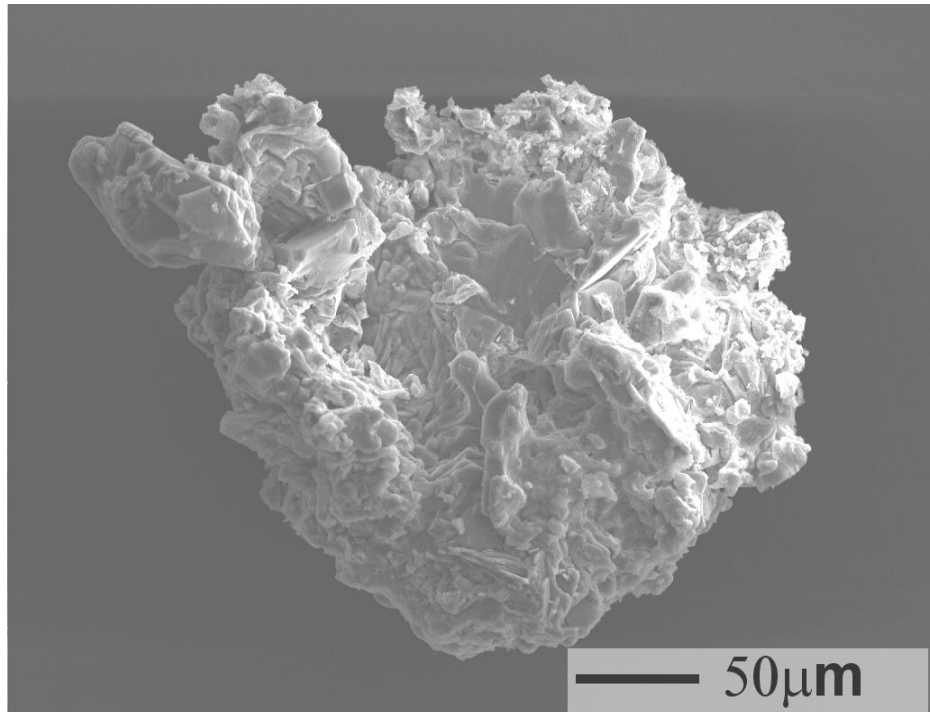
(b) BM082 LL/22: an amorphous mass in which a few fractured cubic and prismatic crystals can be identified.



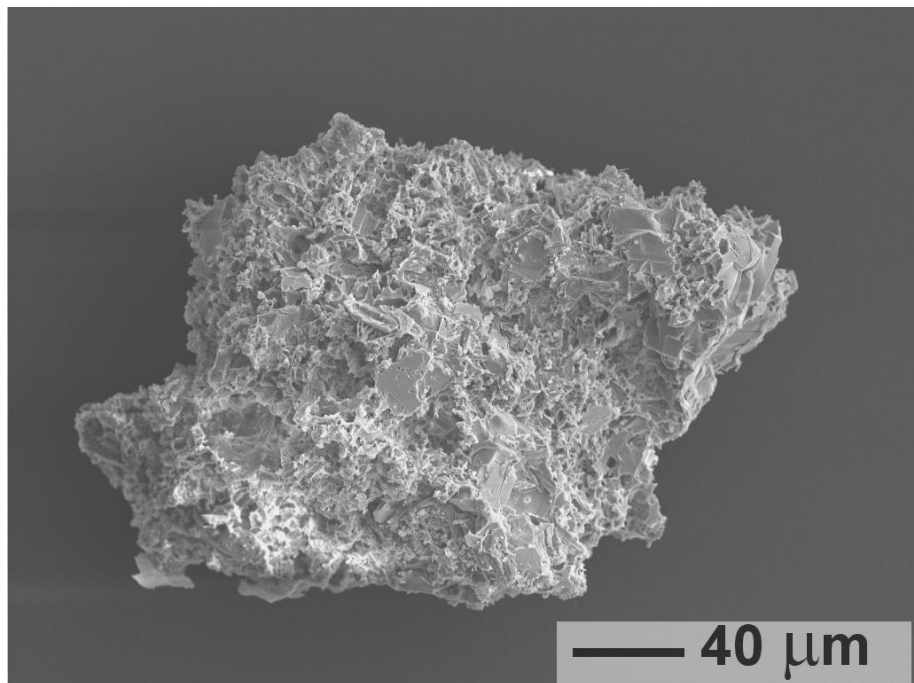
(c) BM070 MM/24: an amorphous mass showing a single fractured crystal face



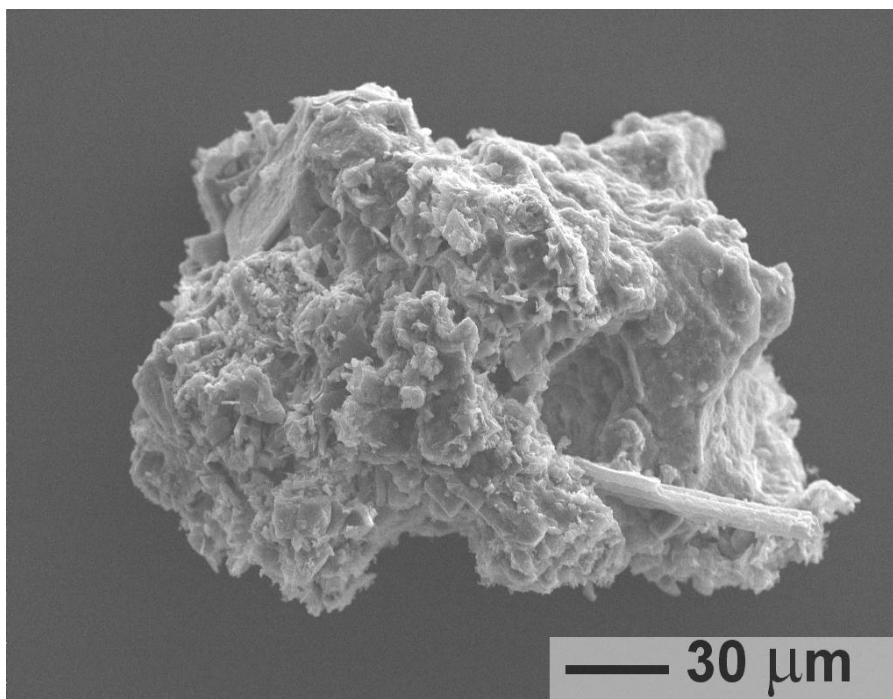
(d) BM065 MM/25: an amorphous mass showing fractured cubic, tabular and prismatic crystals



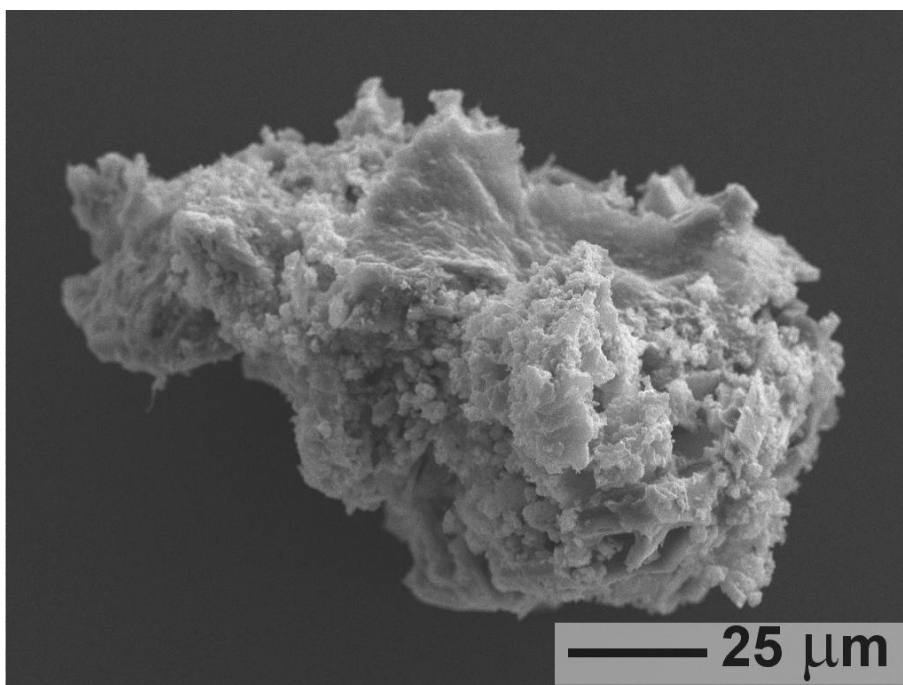
(e) BM080 MM/29: an amorphous mass with few fractured platy, tabular, prismatic and cubic crystals



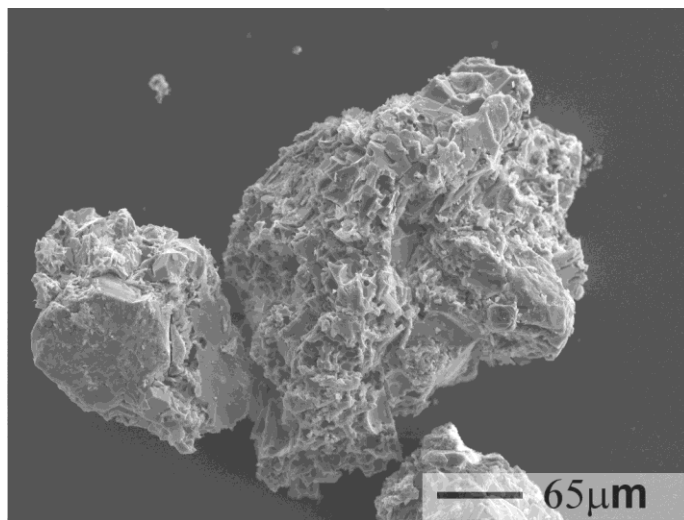
(f) BM089 NN/29: an amorphous mass showing multiple fractured platy, tabular and cubic crystals



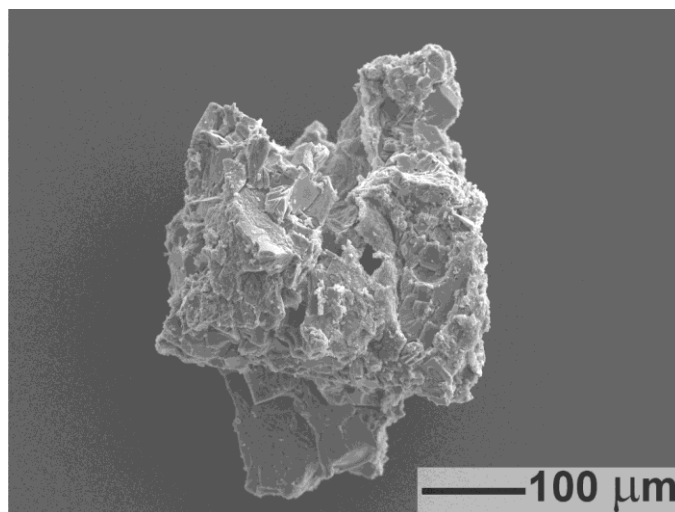
(g) BM054 TT/30: an amorphous mass showing a few fractured cubic crystals and a single compound prismatic crystal



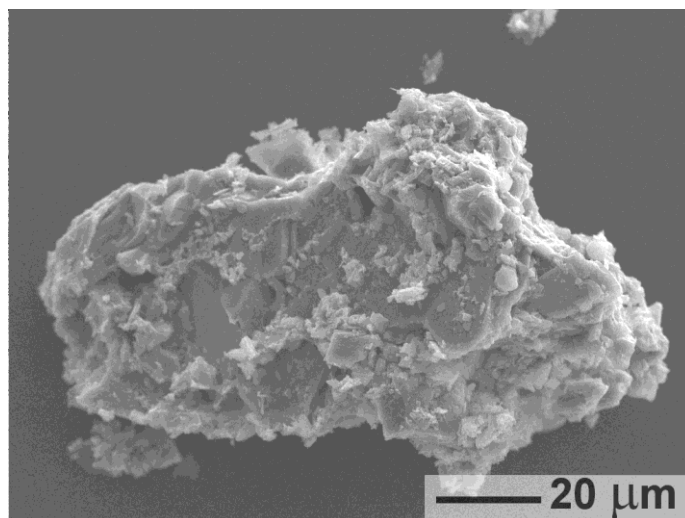
(h) BM086 UU/22: an amorphous aggregate



(i) BM127 VV/15: an amorphous mass showing a few fractured crystal faces



(j) BM136 V/30: an amorphous mass showing a few fractured cubic, platy and tabular crystal faces



(k) West Field: an amorphous mass showing multiple fractured tabular and platy crystal faces

CHAPTER 6

Blue Frit Pellets excavated from Turners Hall Farm near St Albans

... they painted some surfaces with coarsely ground pigments ...

Delamare & Guineau, 1999, 33

6.1 Introduction

In 2002 the St Albans Archaeology Unit was contacted by Verulamium Museum who indicated that they had been shown some high status objects. These objects had been discovered by two metal-detectorists, working a Roman burial site at Turners Hall Farm, near St Albans. Before the site was excavated field walking was organised to collect any artefacts that lay on or near the surface and a geophysical survey undertaken to assess what anomalies lay beneath the soil.

Over the three year period that excavations took place, the St Albans team discovered that the site had firstly been occupied in the Iron Age period and had continued to be occupied through Roman times, during which wealthy owners built a cottage or corridor-type villa. Besides finding rich burials, clay pellet-moulds were also found for producing Late Iron Age coins, suggesting that Turners Hall Farm may have been under the political control of Verlamion (the precursor of Roman Verulamium), an Iron Age town or *oppidum* for the minting of coins (West, 2005). Turners Hall Farm lies some 6 miles north-east of the *oppidum*, shown in Map 4.

Three samples of Egyptian Blue pellets were excavated from different areas on this Iron Age / Roman site. One of the Egyptian Blue pellets (MED04 V1544/926) was found in trench 2 in a layer of silt of Roman occupation at the base of a lynchet, over a possible Iron Age roundhouse. Another Egyptian Blue pellet (MED06 1196/62) was excavated from the lower fill of two large ditches close to, but not on, the actual villa site, possibly near workshops where much metal débris had been found. A third pellet, HYP04 043/25, was also found at Turners Hall Farm, though the position of its location on the site has yet to be identified.

6.2 Analytical Investigations

Semi-quantitative geochemical techniques were employed in order to identify the elemental composition of the three pellets mentioned above, *viz.* MED04 V1544/926, MED06 1196/62 and the third pellet, assigned the designation HYP04 043/25. The two techniques used to analyse these samples were Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) and Scanning Electron Microscopy - Energy Dispersive X-ray Analysis (SEM-EDAX). The methods used in the preparation of these three pellets is fully discussed in Chapter 3. The pellets were examined by naked eye and were also examined under a MEIJI techno RZ zoom Stereomicroscope with a fibre-optic light source to study fine detail. The pellets were weighed, measured and the colour of each pellet was identified using the Munsell Book of Color (Matt Finish Collection) 2001 as a guide. This information is detailed in figure 6.1.

6.3 Results

The LA-ICP-MS and SEM-EDAX analysis indicates the elemental components of each pellet and are shown in figure 6.2. In the pellet HYP04 043/25 (figure 6.2a) there is a high copper content with some tin and smaller amounts of lead. With Egyptian Blue pellet MED04 V1544/926 (figure 6.2b) again there is a high copper content, a little less than in HYP04 043/25 and some tin and lead and a trace of silica. The results for MED06 1196/62 (figure 6.2c) also show a high copper content, a level similar to that of HYP04 043/25, smaller amounts of tin and lead with trace levels of silica.

In the SEM-EDAX analysis silica is identified as the major element in all the three pellets. All three pellets also have moderate amounts of copper and calcium. However, in MED04 V1544/926 (figure 6.2b), unlike the other two pellets, there are trace levels of lead, potassium, magnesium, aluminium, sodium and iron. Trace levels of carbon were detected in MED04 V1544/926 (figure 6.2b) and MED06 1196/62 (figure 6.2c). A difference between the two geochemical analyses is that LA-ICP-MS is unable to detect calcium, whereas the SEM-EDAX is unable to detect the presence of tin in any of these three pellets. Lead is detected in MED04 V1544/926 only.

The results of the LA-ICP-MS and SEM-EDAX analyses are tabulated in figure 6.3 a and b.

6.4 Discussion

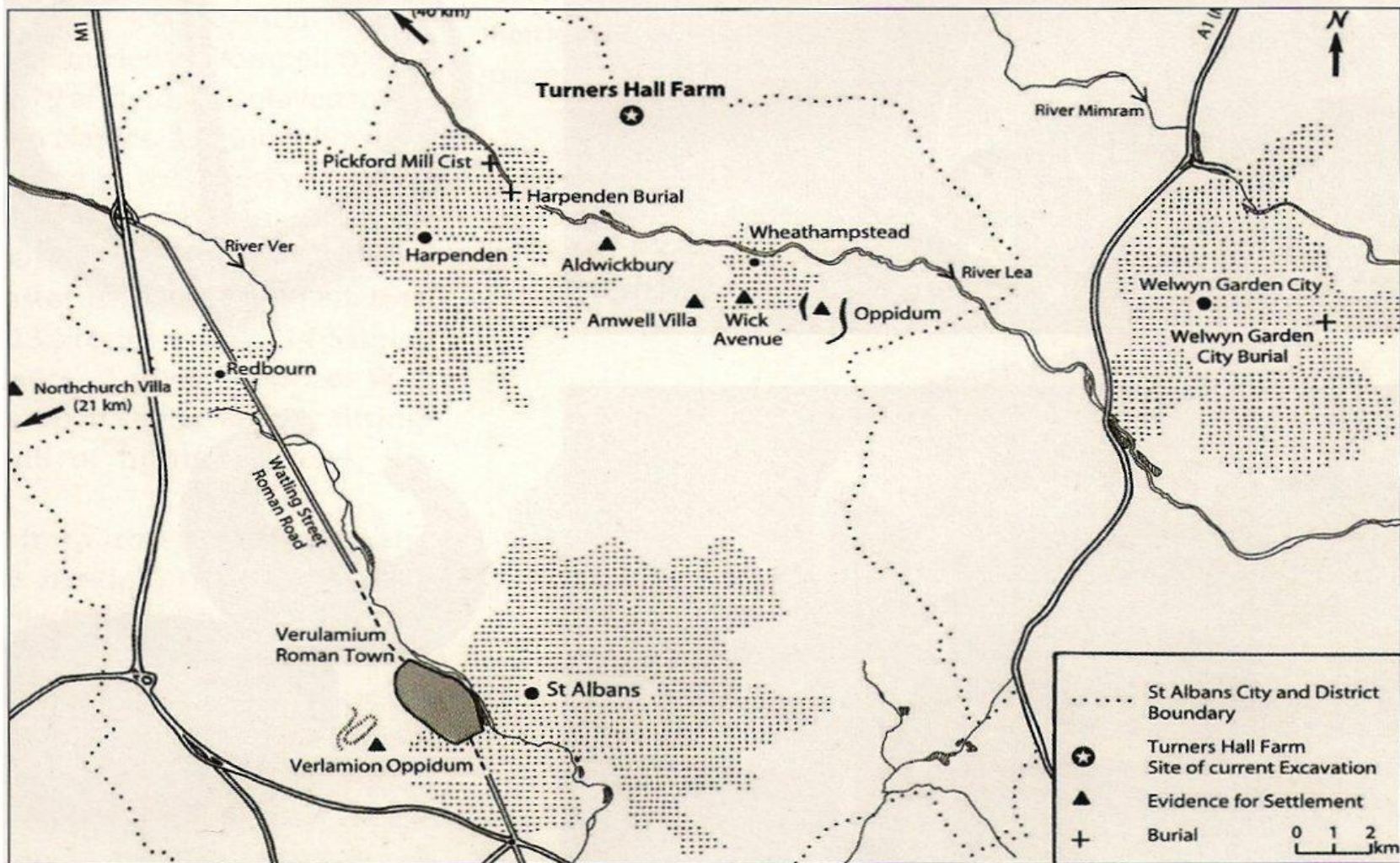
The presence of lead, copper and tin, indicated by the LA-ICP-MS analysis suggests that all three pellets were made from scrap metal. This hypothesis is supported by the knowledge that pellet MED06 1196/62 was found near workshops where metal workings are known to have taken place. If bronze was

used as a scrap metal then it is evident that tin needs to be identified. The combination of trace amounts of carbon, potassium and magnesium is possibly associated with a flux *ie* potash, which may have been used in the manufacture of these pellets. A trace of silica was identified by the LA-ICP-MS technique in two of the pellets. Although the SEM-EDAX analyses identified silica, calcium and copper it was unable to detect the presence of tin and lead in two of the samples although trace levels were detected in MED04 V1544/926.

The microscopic detail of these three pellets suggest that they may all have been manufactured by the same group of artisans. Although the grain sizes differ slightly, the structure and texture of the pellets appear similar, as shown in figure 6.4. Large grains of quartz can be seen in HYP04 043/25 and in MED06 1196/62, but none appear in MED04 V1544/926.

However, when observed under high power microscopy, figure 6.5, (the bar in the top left hand corner represents 50µm), the second picture, MED04 V1544/926 (figure 6.5b) and the third MED06 1196/62 (figure 6.5c) show the presence of quartz grains of various sizes, but none were observed in HYP04 043/25 (figure 6.5a). A single clear washed grain has been detected in HYP04 043/25, which may suggest that this pellet had been made by an expert. However, the two other pellets, not showing washed grains, were possibly made by an apprentice, who would have been affiliated to the master craftsmen

The crystal form of the pellets, HYP04 043/25 and MED 04 V1544/926 is pluristic, with several fractured habits visible. However, pellet MED06 1196/62 shows almost exclusively an agglomeration of fractured crystals with a tabular habit. These are all shown in figure 6.6.



Map 4 showing the relative positions of Turners Hall Farm and the *Verlamion Oppidum*.

With the permission of St Albans Archaeology Unit.

Figure 6.1 Showing the colour, weight and size of the three pellets from Turners Hall Farm



6.1a HYP04 043/25

Weight 1.49g
Dimensions: 12.63 x 11.77
mm

Munsell No. 10B 7/6



6.1b MED04 V1544/926

Weight 2.06g
Dimensions:: 18.36 x 14.88mm

Munsell No. 10B 7/6



6.1c MED06 1196/62

Weight 1.14g
Dimensions: 13.3 x10.95mm

Munsell No. 10B 6/6

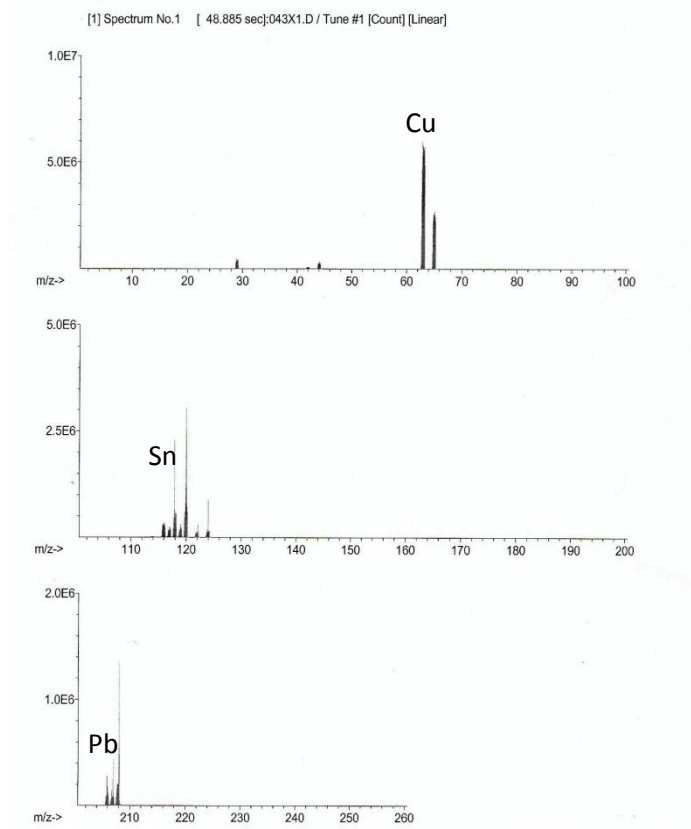
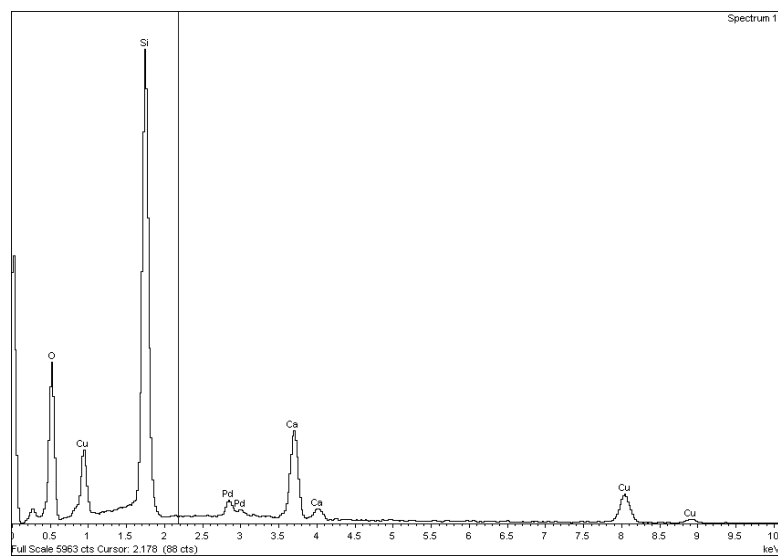
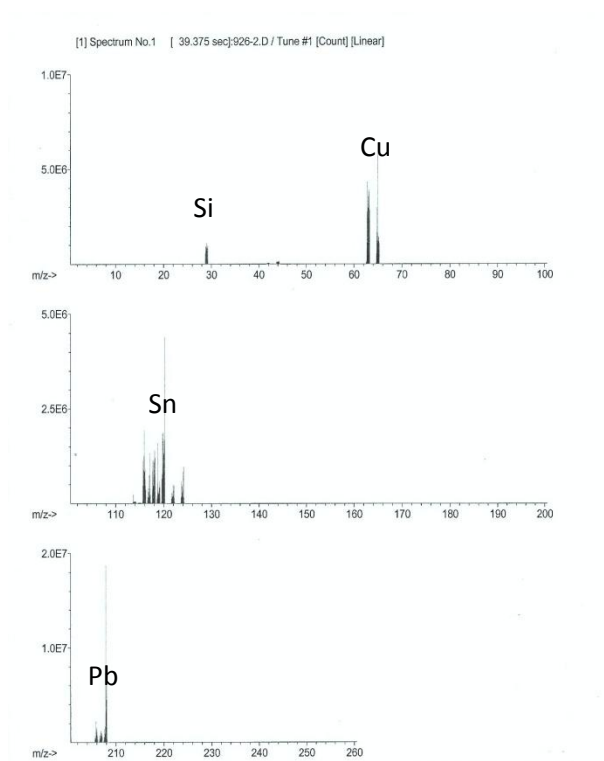
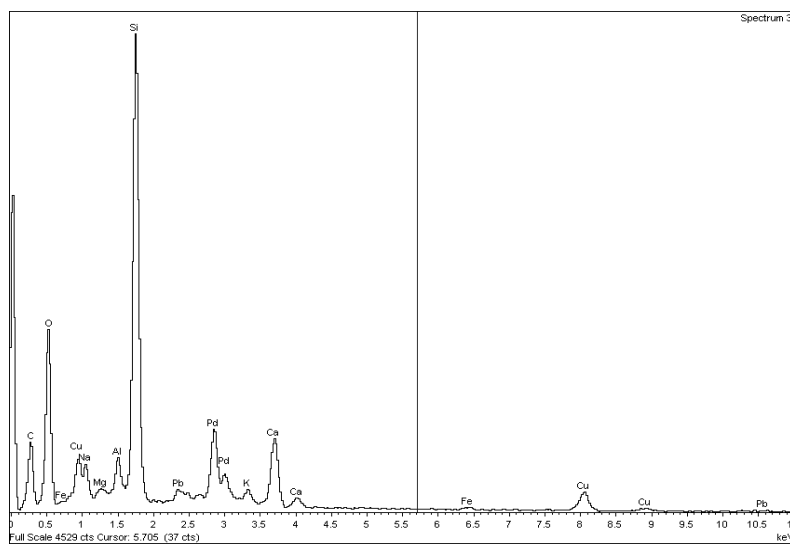
Figure 6.2 a HYP04 043/25**EDX energy spectrum for LA-ICP-MS****EDX energy spectrum for SEM-EDAX**

Figure 6.2b MED04 V1544/926

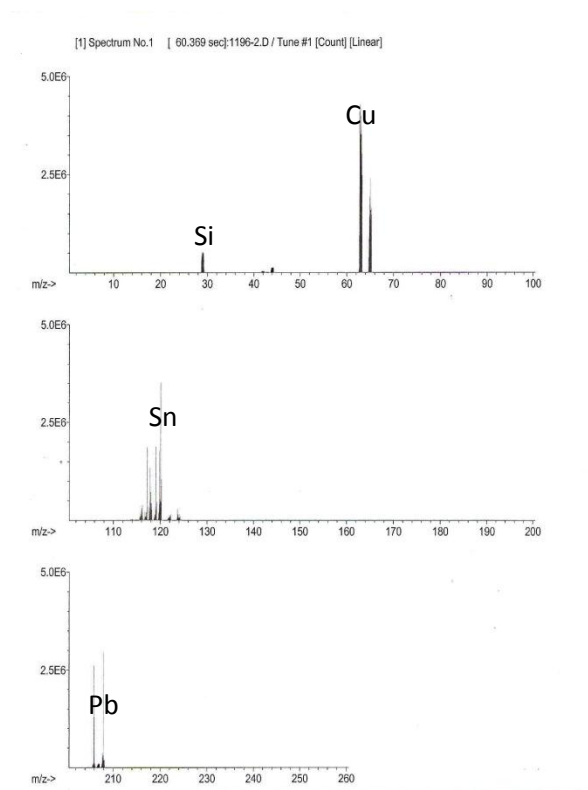


EDX energy spectrum for LA-ICP-MS

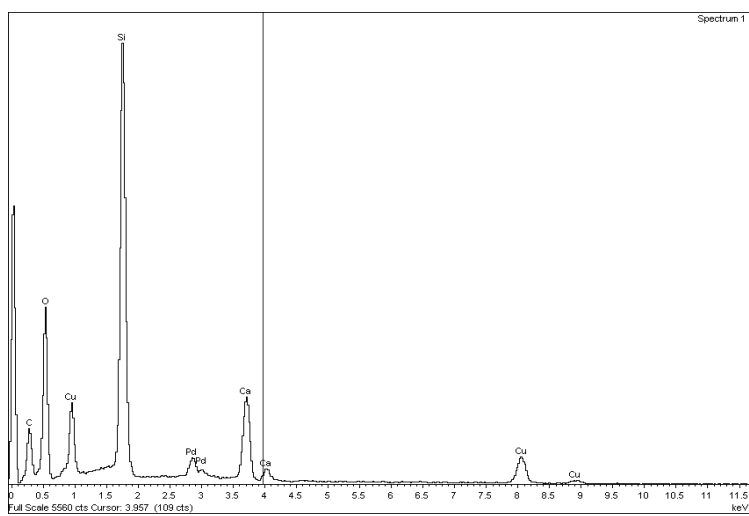


EDX energy spectrum for SEM-EDAX

Figure 6.3c MED06 1196/62



EDX energy spectrum for LA-ICP-MS



EDX energy spectrum for SEM-EDAX

Figure 6.3A

**Summary of elements detected by LA-ICP-MS Analysis
of Egyptian Blue pellets found at Turners Hall Farm**

| | C | Cu | Fe | Si | Pb | Sn | Na | Ca | Ba | K | Al | Mg |
|-----------------------|---|----|----|----|----|----|----|----|----|---|----|----|
| HYP04 043/25 MED04 | | x | | | x | x | | | | | | |
| V1544/926 | | x | | x | x | x | | | | | | |
| MED06 1196/62 | | x | | x | x | x | | | | | | |

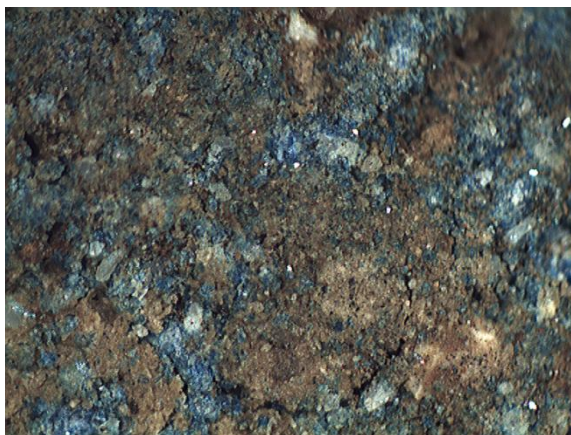
Figure 6.3B

**Summary of elements detected by SEM-EDAX Analysis
of Egyptian Blue pellets found at Turners Hall Farm**

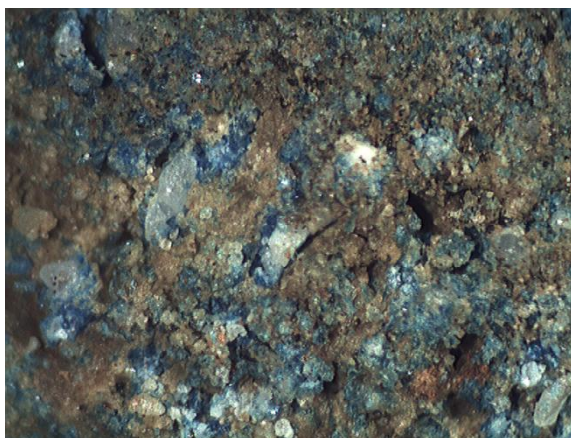
| | C | Cu | Fe | Si | Pb | Sn | Na | Ca | Ba | K | Al | Mg |
|-----------------------|---|----|----|----|----|----|----|----|----|---|----|----|
| HYP04 043/25 MED04 | | x | | x | | | | x | | | | |
| V1544/926 | x | x | x | x | x | | x | x | | x | x | x |
| MED06 1196/62 | x | x | | x | | | | x | | | | |

| | | | | |
|--------------|----|---------|----|-----------|
| KEY : | C | Carbon | Na | Sodium |
| | Cu | Copper | Ca | Calcium |
| | Fe | Iron | Ba | Barium |
| | Si | Silicon | K | Potassium |
| | Pb | Lead | Al | Aluminium |
| | Sn | Tin | Mg | Magnesium |

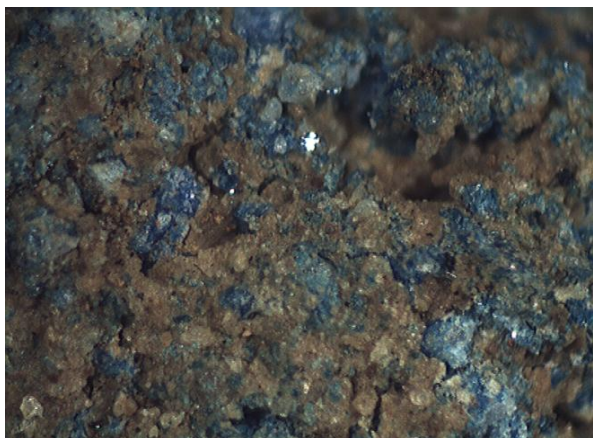
Figure 6.4 Microscopic pictures x 7.5 of the pellets found at Turners Hall Farm



(a) HYP04 043/25

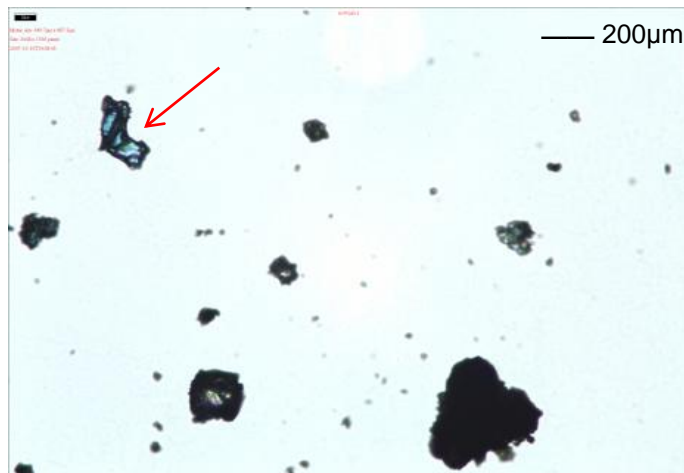


(b) MED06 1196/62



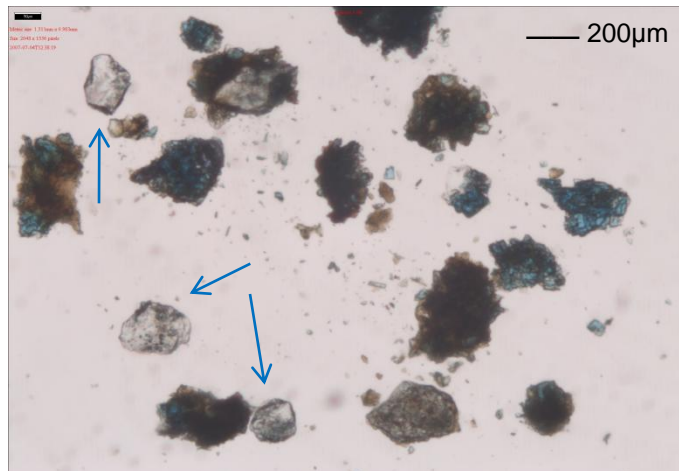
(c) MED04 V1544/926

Figure 6.5 Microscopic examination of grains from the three pellets found at Turners Hall Farm



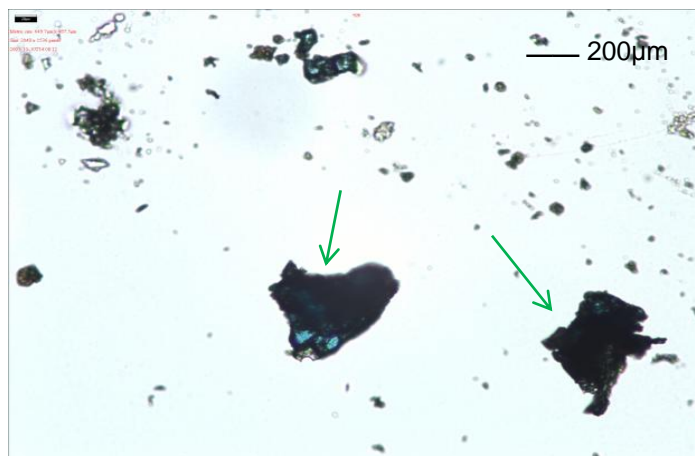
(a) Different grain sizes.

The red arrow indicates a single 'washed' grain for HYP04 043/25



(b) Clusters of different grain sizes

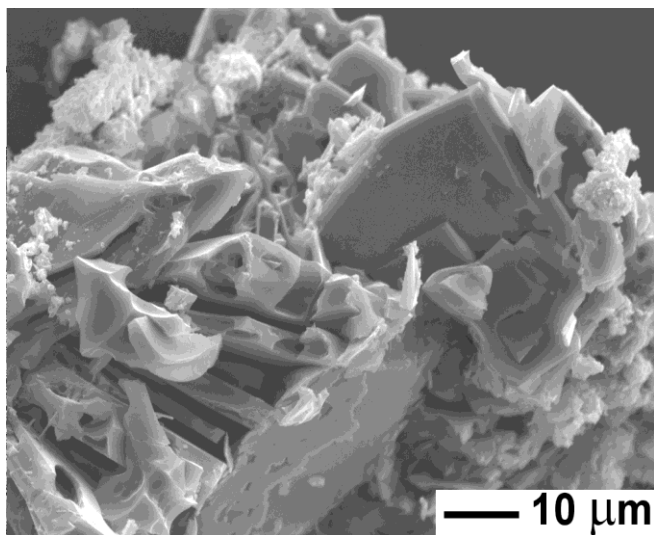
Blue arrows show the presence of quartz from MED06 1196/62



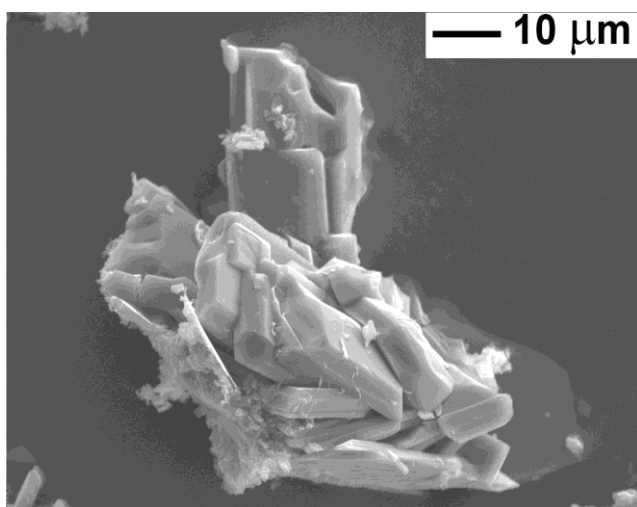
(c) Large well defined grains from MED04 V1544/926

Green arrows show unwashed grains

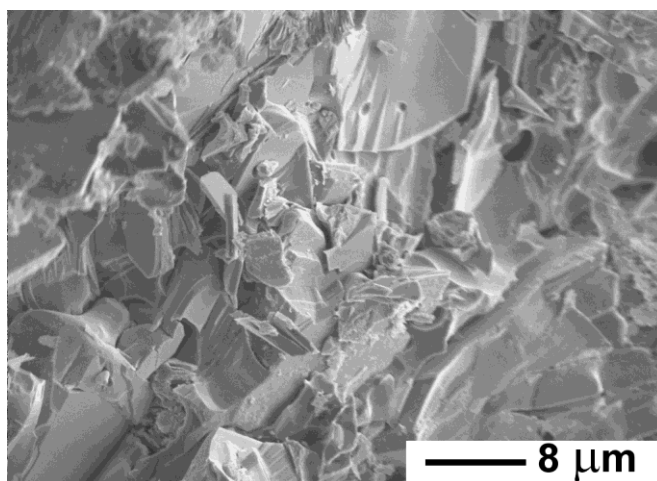
Figure 6.6. Showing the crystal habit of the three pellets from Turners Hall Farm



(a) HYP04 043/25.
A mass of crystals showing large platy and tabular and smaller prismatic with a few acicular habits



(b) Med06 1196/62.
An agglomeration of fractured tabular crystals forms



(c) Med 04 V1544/926.
A mass of fractured crystal faces showing platy, tabular and cubic forms.

CHAPTER 7

Verulamium blue frit pellets

“... is coarsely crystalline and pure blue in color”

Gettens & Stout, 1966, 112

7.1 Introduction

Two large Egyptian Blue pellets were loaned by Verulamium Museum for this research project. Sadly, there is no record indicating when or from where these pellet were excavated in Roman St Albans. However, it is understood that these finds are associated with Sir Mortimer Wheeler's excavations of Verulamium during the 1900s, though it seems that they were not considered important enough to be documented in the original find's records. The location of Verulamium is shown on Map 5.

7.2 Analytical Investigations

Semi-quantitative geochemical techniques were employed in order to identify the elemental composition of these two pellets. The two main methods used to analyse these samples were Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) and Scanning Electron Microscopy - Energy Dispersive X-ray Analysis (SEM-EDAX). The pellets were weighed, measured and the colour of each identified using the Munsell Book of Color (Matt Finish Collection) 2001, figure 7.1. The pellets were also examined under a MEIJI techno RZ zoom Stereomicroscope with a fibre-optic light source to study fine detail. The methods used in the preparation of samples is fully discussed in Chapter 3.

7.3 Results

The elemental composition of the two pellets, Verulamium One and Verulamium Two, as derived from the two geochemical techniques, are shown in the spectra of figure 7.2.

The LA-ICP-MS analysis for Verulamium One shows the presence of copper with smaller amounts of tin and lead and traces of calcium and silica. The record for Verulamium Two shows that copper and tin are the dominant elements, with a smaller amount of lead and a trace of silica. Calcium is noticeable by its absence.

In the SEM-EDAX analysis of Verulamium One, silica is identified as the major element with traces of calcium, aluminium, copper and carbon. Lead and tin were not identified. The results of the SEM-EDAX analysis for Verulamium Two similarly indicates a lack of tin and lead but traces of copper, calcium, aluminium, carbon and a large presence of silica.

The two geochemical analyses suggest that the elemental composition of the two pellets is similar, though in each analytical method the ratios of the different elements identified are characteristic. The elements copper, silica and calcium are present in both samples. However, tin and lead are detected by the LA-ICP-MS analyses but not by the SEM-EDAX.

The results of the LA-ICP-MS and SEM-EDAX analysis is tabulated in figure 7.3a and b.

Both pellets were examined by the naked eye and under a fibro-optic microscope. The structure of grains of the pellets was different: in Verulamium One (figure 7.4a) the grains, seen under the microscope,

were large and cleanly formed, *ie* washed, whereas in Verulamium Two (figure 7.4b) the grains are smaller, ragged and ill-defined in shape, implying that they were unwashed.

The SEM-EDAX images show a clear difference in the texture and crystal form of the two pellets. Figure 7.5a shows a single well defined crystal with a tabular habit from the Verulamium One pellet. This can be contrasted with the ragged conglomerate of crystals found in the Verulamium Two pellet, figure 7.5b, which show fractured cubic, tabular and prismatic habits.

7.4 Discussion

From the above geochemical results it can be seen that the two pellets have a different elemental content. It is not surprising, therefore, that they also differed in texture, structure, and colour. The microscopic examination of the two pellets demonstrates that they have a different surface texture and colour as shown in figure 7.6. The Verulamium One pellet (figure 7.6a) can be seen to be of a rich blue colouration whereas the Verulamium Two pellet (figure 7.6b) is of a much paler colouration.

Furthermore, the counts for the main copper isotopes, ^{63}Cu and ^{65}Cu , differed markedly between samples. In the Verulamium One pellet the average amount (of three runs) of the ^{63}Cu and ^{65}Cu isotopes, derived from the LA-ICP-MS histograms, is 52.7×10^5 and 24.6×10^5 respectively. For the Verulamium Two pellet the corresponding values are 37.9×10^5 and 17.5×10^5 . This data is shown as a histogram in figure 7.6 and indicates that the Verulamium One pellet contains considerably more copper than the Verulamium Two pellet; the amount of copper in a

pellet is closely related to the depth of the blue colouration. It is worth noting that the ratio of the two copper isotopes $^{63}\text{Cu} / ^{65}\text{Cu}$ in both pellets is approximately 2.140; in Verulamium One the ratio is 2.142 and in Verulamium Two the ratio is 2.166 (to three decimal places in each case). This ratio differs somewhat from those reported as typical of copper minerals from historical mines (*ca.* 2.42 – 2.46, Marelli *et al.*, 2010), which itself differs from the ratio (of 2.24) given by Clark in his *New Physical & Mathematical Tables*, 1970). The difference between the experimentally produced ratio and the two published figures is probably due to the analytical limitations of the LA-ICP-MS used in this study.

For the Verulamium One pellet the SEM-EDAX image (figure 7.5a) shows a regularly formed crystal habit and in the microscopic picture (figure 7.4a) the grains are cleanly formed and appear to have the appearance of having been ‘washed’. These two factors suggest that this pellet was likely to have been manufactured by an expert, a master craftsman, who was evidently able to produce such a fine specimen.

Although the elemental composition of the two pellets is similar, the manufacturing process used to produce the Verulamium Two pellet was different. The SEM-EDAX image shows that the crystal habit is totally disorganized and, under microscopy (figure 7.4b), the various grain sizes show that they have a jagged, fractured and ‘unwashed’ appearance. It might well be suggested that this pellet was not made by an expert but by an apprentice - possibly one of the apprentices who was part of the entourage attached to the master craftsman responsible for the manufacture of the Verulamium One pellet.

The LA-ICP-MS analysis indicates, in both pellets, the presence of tin and lead, also copper, which suggests that both pellets may have been made from scrap metal, most probably from bronze scrapings foraged from the metal workshops of the presumed nearby building site.

The Egyptian Blue pellets identified from this site were the result of a utilitarian method of manufacture, using copper associated with small amounts of tin and lead from discarded pieces of scrap metal instead of the more expensive copper filings recommended by Vitruvius (Book VII, XI,1). An alternative, though more expensive, approach would be to include a mineral such as malachite instead of copper filings.

Figure 7.1 Showing the weight, size and colour of the two Verulamium pellets



7.1a Verulamium One

Weight: 7.38g

Dimensions: 30.42 x 23.22 mm

Munsell No. 5PB 5/6



7.1b Verulamium Two

Weight: 10.63g

Dimensions: 32.66 x 27.34 mm

Munsell No. 10B 6/4

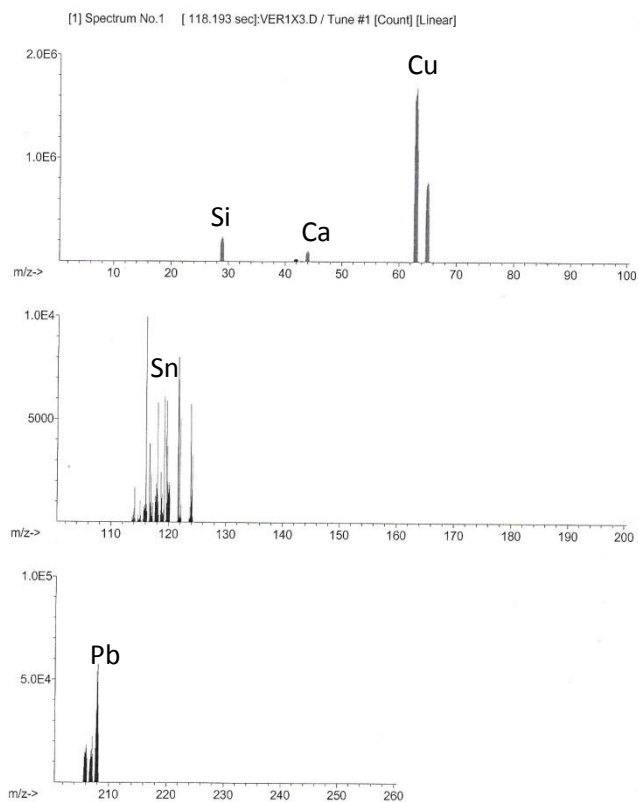
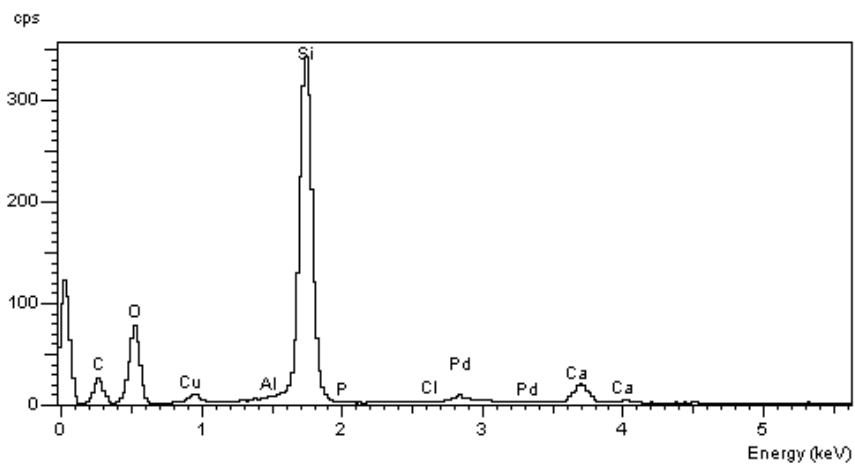
Figure 7.2 a Verulamium One**EDX energy spectrum for LA-IPC-MS****EDX energy spectrum for SEM-EDAX**

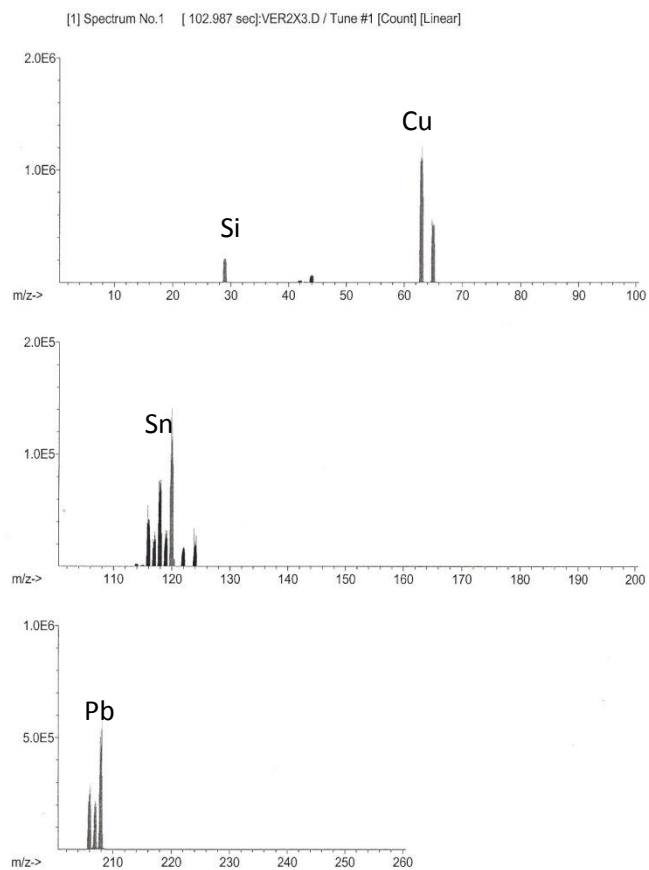
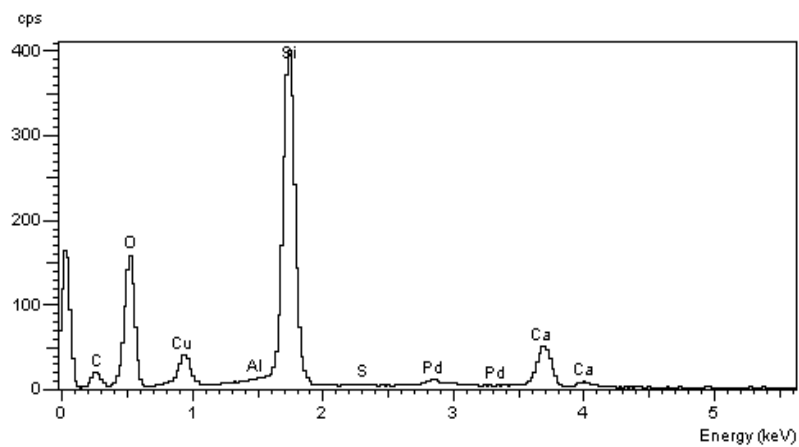
Figure 7.2b Verulamium Two**EDX energy spectrum for LA-ICP-MS****EDX energy spectrum for SEM-EDAX**

Figure 7.3A

Summary of elements detected by LA-ICP-MS Analysis of Egyptian Blue pellets found at Verulamium

| | C | Cu | Fe | Si | Pb | Sn | Na | Ca | Ba | K | Al | Mg |
|----------------|---|----|----|----|----|----|----|----|----|---|----|----|
| Verulamium-One | | x | | x | x | x | | x | | | | |
| Verulamium-Two | | x | | x | x | x | | | | | | |

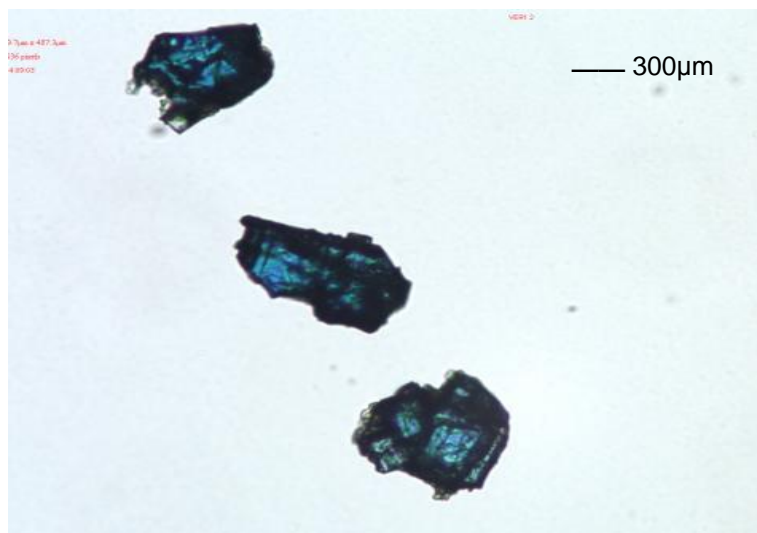
Figure 7.3B

Summary of elements detected by SEM-EDAX Analysis of Egyptian Blue pellets found at Verulamium

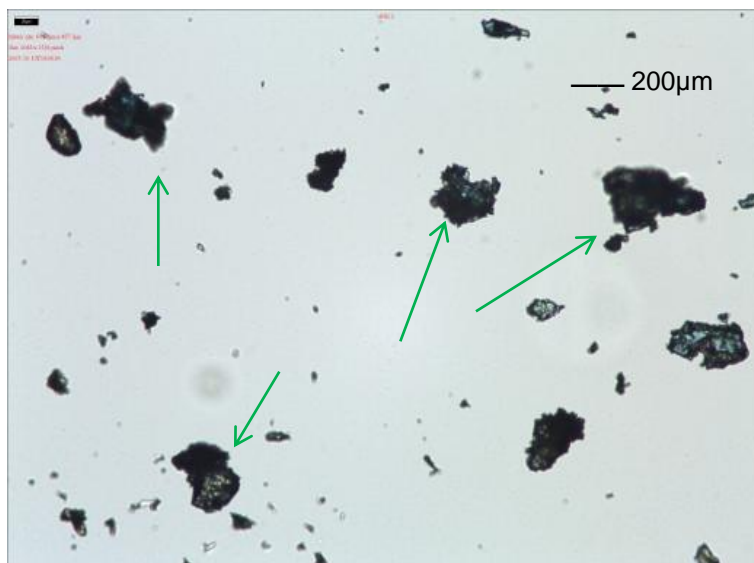
| | C | Cu | Fe | Si | Pb | Sn | Na | Ca | Ba | K | Al | Mg |
|----------------|---|----|----|----|----|----|----|----|----|---|----|----|
| Verulamium-One | x | x | | x | | | | x | | | x | |
| Verulamium-Two | x | x | | x | | | | x | | | x | |

| | | | | |
|--------------|----|---------|----|-----------|
| KEY : | C | Carbon | Na | Sodium |
| | Cu | Copper | Ca | Calcium |
| | Fe | Iron | Ba | Barium |
| | Si | Silicon | K | Potassium |
| | Pb | Lead | Al | Aluminium |
| | Sn | Tin | Mg | Magnesium |

Figure 7.4 Microscopic examination of grains from the two Verulamium pellets

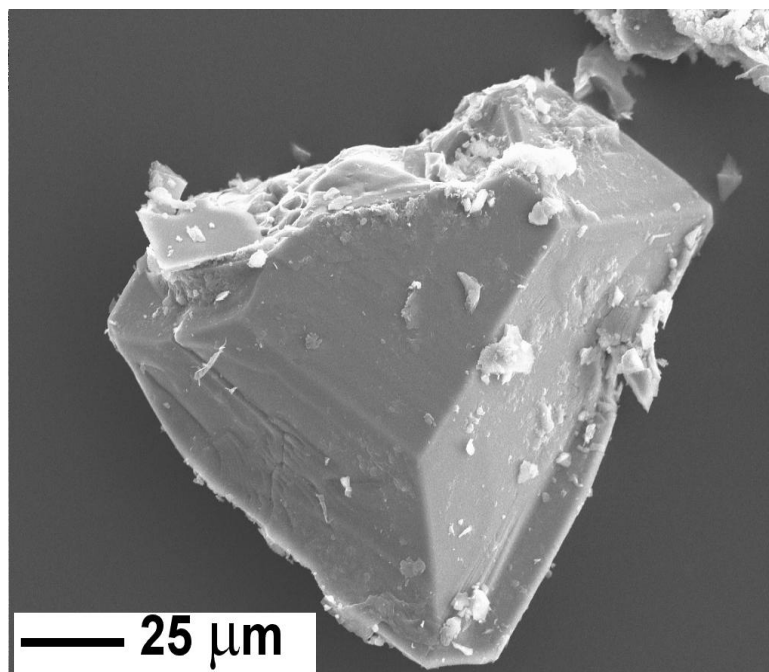


7.4a Verulamium One shows large cleanly formed washed grains

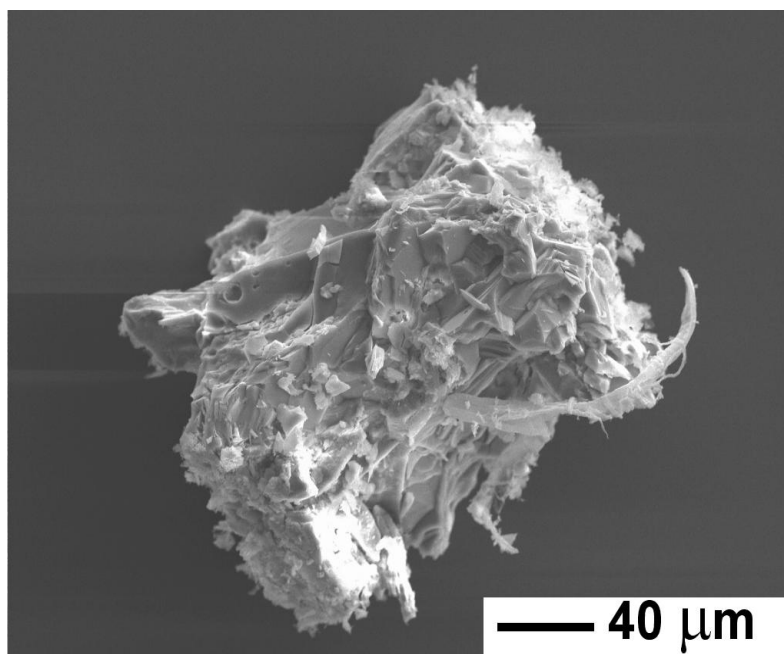


7.4b Verulamium Two. Green arrows show a cluster of different sized unwashed grains

Figure 7.5 Showing the crystal habit of the two Verulamium pellets

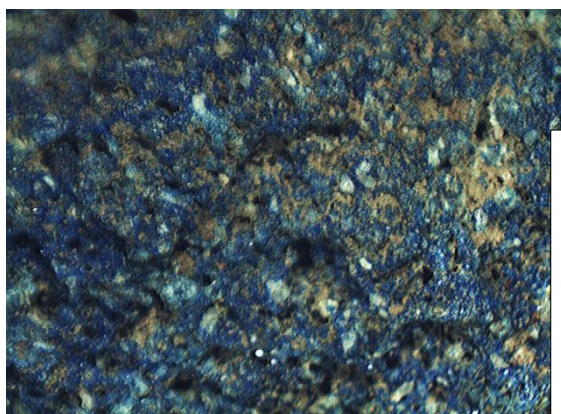


7.5a Verulamium One: showing a single tabular crystal



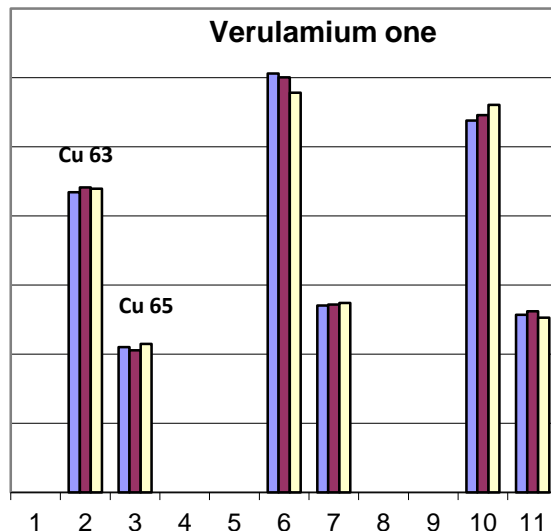
7.5b Verulamium Two: an amorphous mass showing a few fractured cubic, tabular and prismatic crystals

Figure 7.6 Surface structure (magnification x 7.5) and isotopes ^{63}Cu and ^{65}Cu contents of the two Verulamium pellets



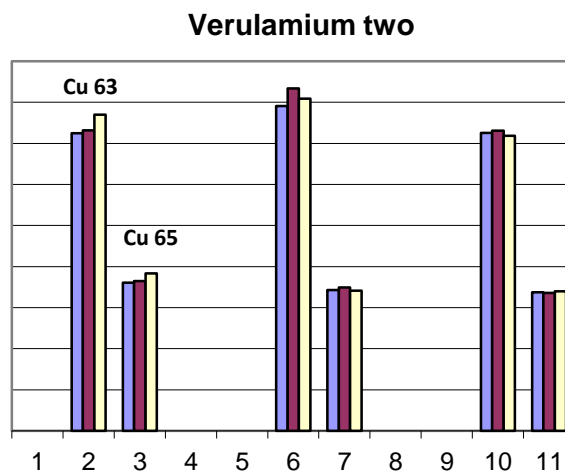
Verulamium One - microscopic picture showing dark blue grains

7.6a Verulamium One - LA-ICP-MS data showing Cu content from isotopes ^{63}Cu and ^{65}Cu



Verulamium Two -microscopic picture showing pale blue grains

7.6b Verulamium Two - LA-ICP-MS data showing Cu content from isotopes ^{63}Cu and ^{65}Cu



CHAPTER 8

Fragments of Blue and Green Painted Wall Plaster found in Verulamium Park, St Albans

The brilliant colours, which the patron supplies at his own expense to the painter...

Pliny, Book XXXV, 12

8.1 Introduction

During the summer of 2008 the St Albans District Archaeology Unit, led by Simon West, organised an excavation of a small area of a high status town house in Verulamium Park. The house, constructed over the period AD 150 to 300, consisted of at least thirty-three rooms with wall-paintings, mosaics and hypocausts. Sir Mortimer Wheeler and his wife had excavated this area during the 1930s. The St Albans Unit had expected to find the remains of one of the mosaic floors, but this eluded them. However, whilst in the process of back filling the hypocaust, seven small fragments of blue and green painted plaster were recovered. The size of the fragments ranged from 16 to 25 mm across. These seven small painted plaster specimens were subsequently analysed in an attempt to determine the type of pigment used; two of these fragments were further studied to ascertain the nature of the binding agent that had been employed.

The use of a binding material or medium, mixed with a ground pigment, can be traced as far back as the Palaeolithic period when traces of plant and animal oils were found to have been used as a binding agent (Bahn & Vertut, 1997). Lucas (1934) mentions that the Egyptians used both size (made from animal glue) and

albumin (egg white) to enable pigments such as Egyptian Blue to adhere to wet or dry plaster. Laurie (1967) noted that the Egyptians used gum arabic as a binding agent and Spurrell (1895), when studying fragments of painted plaster from Kahun (Twelfth Dynasty), found that albumin and gum arabic were used as a medium and that acacia gum had been used at Tell el-Amarna. He also recorded that albumin and gelatine were used as the binding agent in the paintings of Akhenaton and his daughters. Forbes (1955) mentions the use of animal glue, egg white and beeswax. Chromatographic analysis of a sample from a Roman building beneath the cathedral in Köln revealed traces of amino-acids which Davey & Ling (1982) suggests indicated that the pigment may have been mixed with an animal size. Pliny (quoted in Davey & Ling, 1982) informs the reader that ... *the finest size is made from the ears and genitals of bulls ... the most reliable variety... comes from Rhodes and is used by painters and physicians*. Vitruvius mentions that the use of an oil mixed with hot wax was used as a binding material (Book VII, IX, 3).

Another medium or binding material that was used to ensure that the ground pigment would adhere to the surface to be painted, is beeswax. Its use, as a binder can be traced as far back as the Eighteenth Dynasty (Spurrell 1895). Lucas also mentions that wax may have been applied as a protective coat to a finished painting. Sir Flinders Petrie (quoted in Lucas, 1934) found that beeswax was used ... *as a filling of the hieroglyphs on the red granite coffin of Ramesses III*. It was during the late 1890s whilst analysing pigments for Petrie, that Russell discovered the use of beeswax as a binding material on the Greco-Roman fragments found at Hawara. He claimed that the pigments used were of great interest as they had been ... *mixed with a wax* ... [and may appear to be similar to] ... *the colours used by the great Greek artists* (Russell, 1892). According to Pliny (Book XXXV, 123) the Greek artist Pausias of Sicyon became famous for producing paintings using the encaustic technique where

ground pigments were added to wax heated by the sun or on a hot plate (Forbes, 1955) which was then ... *burnt in...*(Pliny, Book XXXV,122) to the prepared plaster. Forbes goes on to say that ... *by the time of Apelles a very adequate palette had been acquired with which paintings could be made which surpassed frescoes and tempera paintings in depth and richness of colour* (Forbes, 1955).

Studies were undertaken by Scott and colleagues (2002) to ascertain what type of pigment (and, possibly, what type of binding material) had been applied to the décor of nine Egyptian cartonnage fragments obtained from the Petrie Museum. These fragments dated from the late Old Kingdom (*ca.* 2250 BC) to the early Roman period, *ie* first to second century AD. These fragments were analysed using GC-MS, XRD, SEM-EDX, FTIR and enzyme – linked immuno-sorbant assay (ELISA). The results indicated that a plant gum, animal glue and egg had been used as media, though it was unclear whether the wax detected from these artefacts was indeed the original wax medium or wax that had been added as a protective coating. Another possibility recognized by Scott and colleagues is that it was the wax that Petrie had used to ... *steep his Egyptian artefacts into locally obtained beeswax before sending them to England...*

An in depth study of the pigments and binding media used in ancient paintings found in Alexandria and at other Egyptian sites was undertaken by El Salam in 2011, using GC-MS and Infrared Spectroscopy (FTIR). He questions the use of albumin as a binding material but agrees with Lucas (1934) that gum and glue were used in the Egyptian paintings. He notes that the pigments, with their binding material, would have been exposed to the elements, over thousands of years and that chemical changes would almost certainly have taken place. According to El Salam (2011, 206) GC-MS was one of the ideal techniques to identify organic and other materials that were used as binding media and that the sample ... *should be clean so as to avoid any contamination which would affect the results ...*

In 2012 Casoli & Santoro attempted a study of the pigments and the binding media used in the fresco paintings obtained from different rooms of the *Insula del Centenario* at Pompeii, using Fourier Transform Infrared (FT-IR) and Gas Chromatography-Mass Spectroscopy (GC-MS). Unfortunately, their studies were only able to record details of the modern media, such as wax, egg and animal glue that had been used in previous restoration work for protective purposes; it was not possible to identify the nature of the original media.

8.2 Methodology

Great care was taken when using a number 15 scalpel blade to remove minute samples (weight $\leq 0.1\text{g}$) of pigment from each of the seven painted plaster fragments. Each of these minute samples were mounted on a 12mm aluminium pin stub for SEM-EDAX analysis. Additionally, one of the painted plaster fragments, identified as HYPO8/06, was placed, intact, on a metal disc and inserted into the PANalytical X'Pert ProX-ray diffractometer chamber for XRD analysis.

In addition, an attempt was made to identify the binding material used on two of the seven fragments, namely HYPO8/B and HYPO8/D. Minute samples, (0.03g) and (0.015 g) respectively, were taken from these two fragments and prepared for analysis via GC-MS. Contemporary materials were used as standards: thus weighed beeswax (0.04g) and measured, unrefined, linseed oil (1ml) were prepared and analysed in a manner identical to that to which the ancient specimens had been subjected.

The methods used in the preparation of the painted fragments is fully discussed in Chapter 3.

8.3 The seven St Albans fragments : attempted pigment identification

The semi-quantitative geochemical technique, SEM-EDAX, was employed in order to identify the pigments used in the seven small fragments of painted plaster. The fragments were also examined under a MEIJI techno RZ zoom Stereomicroscope with a fibre-optic light source to study fine detail.

For each of these blue and green painted fragments (recorded as figures 8.1a to 8.1g) details are shown of the painted fragment itself, the SEM-EDAX spectra, and finally its crystal form is noted. Also recorded is an approximation of the dimensions of the fragment and an indication of its colour, identified using the Munsell Book of Color (Matt Finish Collection) 2001.

Results obtained from the SEM-EDAX analysis of the blue and green painted fragments indicate that different pigments were used in the interior decoration of the plastered walls. However, since the fragments were obtained from a back-filled trench it is not possible to place the fragments in particular rooms in the high status house.

Fragment: HYP08/06. The sample (figure 8.1a) shows a blue, gritty and granular surface in which a few bright blue granules stand out against a paler blue background and the clearly visible plaster layer. The SEM-EDAX spectra of this fragment shows that silica, copper, calcium and a small amount of aluminium were present. When examined under the fibre-optic microscope minute crystals could be seen which appear to have a sandy texture. The SEM image for this fragment shows a range of euhedral crystal forms: pyramidal, cubic and platy habits are identifiable.

Fragment: HYPO8/A. This sample (figure 8.1b) shows a fine smooth green surface. The SEM-EDAX spectra identified the presence of silica with small amounts of copper and calcium. A single tabular crystal form can be identified

set against what appears to be a single crystal with a bladed habit in an otherwise amorphous assemblage.

Fragment: HYPO8/B. This fragment (figure 8.1c) shows a fine smooth green surface colour that is both darker and thicker than that of HYPO8/A. The SEM-EDAX spectra is similar to that of HYPO8/A except that there is also a slight trace of iron. The crystal habit is predominantly acicular with what appears to be a few pyramidal and prismatic forms.

Fragment: HYPO8/C. The surface of this fragment (figure 8.1d) shows a fairly thick, smooth blue colouration; within the few slightly rougher areas of this surface there are a few scattered bright blue granules. Beneath the surface colouration is a much thicker layer of a red under colour. The SEM-EDAX spectra from the uppermost (blue layer) showed the presence of silica with smaller amounts of aluminium, calcium and iron. The crystal form is anhedral, with only a single aggregate being identifiable.

Fragments: HYPO8/D & HYPO8/E. Both these fragments (figures 8.1e and 8.1f respectively) show a fine blue surface in which both pale and bright blue granules can be identified. The SEM-EDX spectra show that both have the same elements present, *viz.* silica, iron, copper, lead, magnesium, sodium, calcium, potassium and aluminium. In both samples there is also a trace of chlorine which may suggest surface contamination. The crystal form of both fragments is subhedral. Fragment HYPO8/D shows some fractured tabular and platy habits and a single example of a pinacoid face; fragment HYPO8/E shows a single large tabular crystal with several crystals showing fractured tabular or platy habits.

Fragment: HYPO8/F. The very finely granulated surface of this fragment (figure 8.1g) is unique in that it clearly demonstrates two distinct hues. The upper colour is a much darker blue than the lower covering. The SEM-EDX spectra shows the presence of silica, calcium, copper, aluminium, lead, magnesium and

sodium. A single large crystal showing a tabular habit and a crystal with a fractured cubic habit are clearly visible, together with a few scattered fragments.

The elemental composition, detected by SEM-EDAX analysis, of the seven fragments of blue and green painted plaster found at Verulamium Park are tabulated in figure 8.2.

8.4 Further studies on two of the St Albans fragments

In addition to the above exercise, two fragments were subjected to further analyses: firstly, in an attempt to confirm its mineral composition HYPO08/06 was subjected to XRD analysis and, secondly, in an attempt to identify the binding agent that had been used GC-MS analysis was employed to investigate the fragments HYPO08/B and HYPO08/D.

Figure 8.3 shows the results of the XRD analysis of fragment HYPO08/06. Somewhat unexpectedly the results clearly suggest that a form of the relatively rare mineral diopside, $\text{Cu}_{0.6}(\text{SiO}_3)(\text{H}_2\text{O})_6$, was present. This is found as a secondary mineral in oxidized zones of copper deposits, particularly in arid regions (Mondadori, 1991). The process of its formation is said to be extremely complex. Traces of this uncommon mineral have been found as ... *particles of emerald-like diopside* ... on one of the eyes from the Neolithic sculptures found in the Nahal Hemar Caves above the Dead Sea (Kingery *et al.*, 1988). There is however no evidence of the use of diopside in Roman Britain, and there are no major sources of this mineral in the area occupied by the then Roman Empire. Given this, and the fact that the fragments have been buried for many centuries, the presence of diopside here is almost certainly the result of post-burial secondary alteration and mineral formation, although the exact mechanism of diopside formation in these fragments remains unclear.

In a second investigation minute samples were taken, from the two fragments, for GC-MS analysis in an attempt to detect whether a wax or an oil (or both) had been used as the binding material with the coloured pigments on these fragments.

Modern day samples of linseed oil (figure 8.3a) and unrefined beeswax (figure 8.3b) were analysed by GC-MS using the same column and temperature as had been used to analyse the minute samples from the two fragments. Figures 8.3c and 8.3d show the results of the GC-MS analysis of the fragments HYPO08/B and HYPO08/D respectively.

Various studies show that when analysing samples of modern day linseed oil the ratio of free fatty acids, such as palmitic (C_{16}) and stearic acid (C_{18}), can vary according to the strain or variety of the crop and according to the season (Mills & White, 1999). Linseed oil is dominated by lighter (*ie* lower molecular weight) compounds which are less likely to be preserved and over a period of time degrade more rapidly than those heavier (*ie* higher molecular weight) compounds such as beeswax (Mills & White, 1999).

Beeswax is chemically complex and is mainly composed of odd-numbered hydrocarbons whose molecular weights range from C_{21} to C_{33} and even-numbered free fatty acids (C_{22} to C_{30}), (Regert *et al.*, 2001), together with esters which range from C_{40} to C_{50} (White, 1978). According to Regert (*ibid.*) beeswax is very difficult to identify in paintings that have been preserved on archaeological sites. He also suggests that any such identification would require chemical analysis and that ... *The chromatographic profile of ancient beeswax often presents significant differences to that of contemporary beeswax due to the degradation of this material through time.*

From the GC-MS results of HYPO08/B and HYPO08/D it proved extremely difficult to identify the nature of the binding material that had been used in applying the

pigment to lime mortar. The results from the green painted sample, HYP08/B, (figure 8.3c) show a ‘hump’ in the chromatogram known as an Unresolved Complex Mixture (UCM). There is a wide spread of low molecular weight molecules implying the presence of aliphatics. There is also a wide range of regularly spaced peaks as well as many indications of heavier compounds (C_{21} to C_{30}) which suggests that it may be a wax or possibly a mixture of, for example, beeswax and an oil. Pliny (Book XXXIII, 122) mentions ... *wax melted with olive oil and applied by means of [a] brush ... while it is still hot ...* It is possible that the green pigment was prepared in a similar fashion before being applied to the lime mortar.

The results of the chromatographic study of the blue painted sample, HYDP08/D, (figure 8.3d) is different. The range of peaks is narrow and may suggest the presence of aromatic compounds, with the UCM more defined than that shown in the HYD08/B chromatogram. It is difficult to determine what type of binding material had been used in the preparation of the blue pigment. However, the relative scarcity of heavier compounds and the dominant presence of shorter fatty acids such as palmitic acid, (Stacey, 2008) suggests that an oil, rather than a wax, was the most likely binding medium to have been used.

8.5 Discussion

The painted fragments obtained from the back-fill of the hypocaust from Wheeler’s excavation of a high status town house in Verulamium Park suggest that a variety of different blue and green pigments had been applied to the wall paintings. The thickness of the pigment also varied which might suggest that more care was taken when applying the pigment to some wall-paintings than to others. [It is possible that, *if* the blue pigment (HYPO8/06) were azurite and the green pigment (HYP08/B) malachite, both could possibly have been obtained

from the Roman mine of Pot Shaft at Engine Vein, Alderley Edge (Timberlake, 1999)]. The possible presence of expensive pigments, such as azurite and malachite, and the thickness to which the pigment had been applied to the plaster, would suggest that these fragments may have come from an expensive panel painting or vignette. Such a painting would have been executed by the artist who had been commissioned by a wealthy entrepreneur to decorate the internal walls of this high status building.

The SEM-EDAX results may indicate, at a chemical level, that the synthetic pigment, Egyptian Blue, could have been used on all the fragments apart from HYP08/C, this latter fragment being the only one not to contain copper. Fragments HYP08 /D, HYP08 /E and HYP08 /F, have an almost identical elemental composition and these samples of Egyptian Blue pigment would seem to have been derived from pellets manufactured from components that included scrap metal. The two green fragments, HYP08 /A and HYP08 /B, having silica, copper and calcium, and in the case of the latter fragment iron also, could have been painted with an Egyptian Green pigment. Interestingly, when HYP08 /B was subjected to XRD analysis the mineral diopside, CaSiO_3 , was identified whereas the mineral copper wollastonite, $(\text{CuCa})_3\text{Si}_3\text{O}_9$, was not. Pagès-Camagna and Colinart (2003) claim that this latter mineral is diagnostic for Egyptian Green. Furthermore, the SEM-EDAX analysis is qualitative, not quantitative and does not, therefore, permit a description of the relative quantities of the ingredients: it is known that when excess calcium, in the form of lime, calcium carbonate or even gypsum, is added to the Egyptian Blue ingredients then the resulting pigment will often show a distinctly greenish hue (Jaksch, *et al.*, 1983). Use of Egyptian Green as a pigment is discussed in more detail on pages 56 to 59, Chapter 2. Having stated this, it should be noted, however, that fragment HYP08 /B does demonstrate a markedly dark green hue. However, the results, as a whole, demonstrate that it is impossible to be

absolutely certain which pigments were used on the fragments. This difficulty has been aggravated by weathering, degradation and possible contamination of the sample fragments. The only mineral identified with certainty (diopase) was not used in the production of a pigment for use on these Verulamium paintings.

An attempt using GC-MS to identify the binding materials used in HYP08/B and HYPO08/D proved inconclusive. It was not possible to determine definitively whether an oil or a wax, or a combination of the two, had been used. However, the clear difference of the chromatograms, in samples that have been subject to similar burial and weathering conditions, indicates that different binding materials (or combinations of different binding materials) may have been used on each fragment.

Although not available to the author it is recognized that the use of a polarizing microscope would have aided identification of some, at least, of the crystals found in the original paintings represented by the Verulamium fragments.

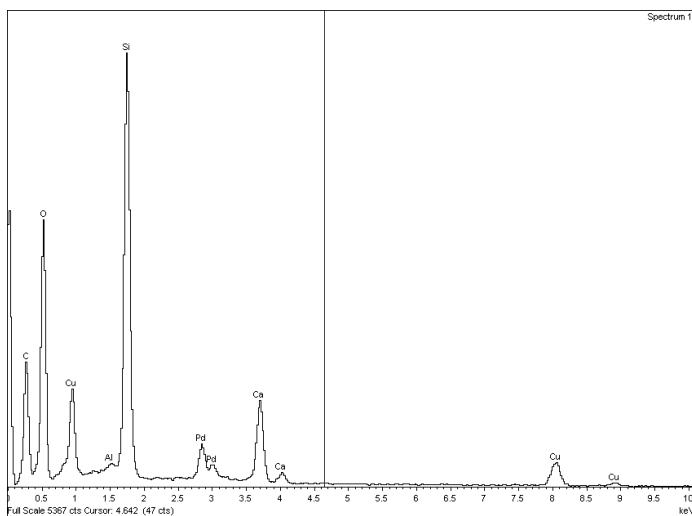
Figure 8.1a HYP08/ 06



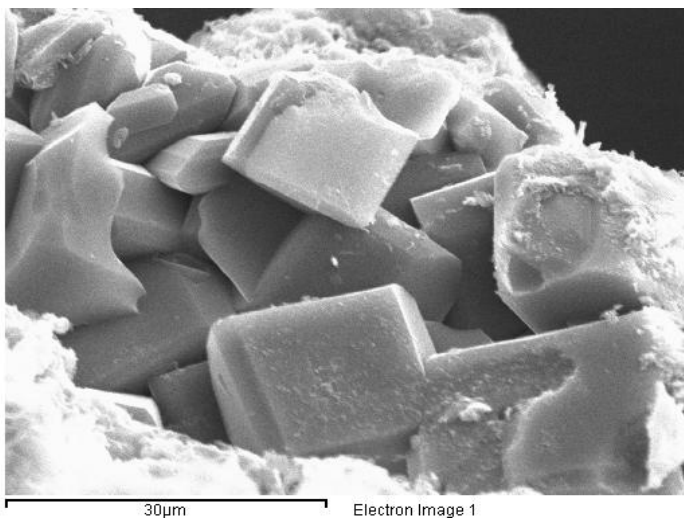
Painted area: 15 x 11 mm

Colour: Blue

Munsell No. 5PB 5/6



EDX energy spectra for SEM-EDAX



Crystal form showing pyramidal, cubic and platy habits

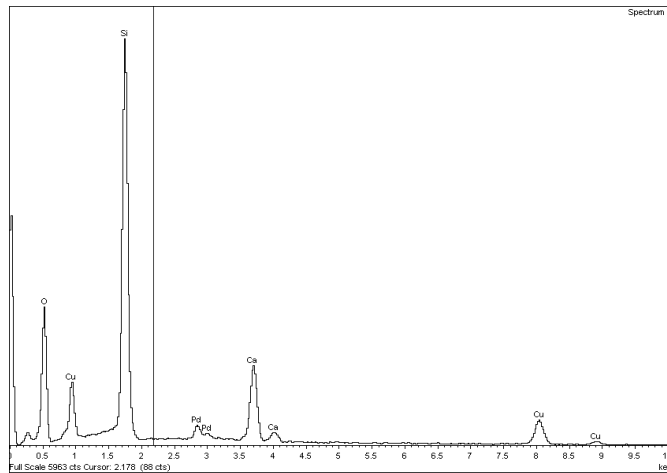
Figure 8.1b HYP08/A



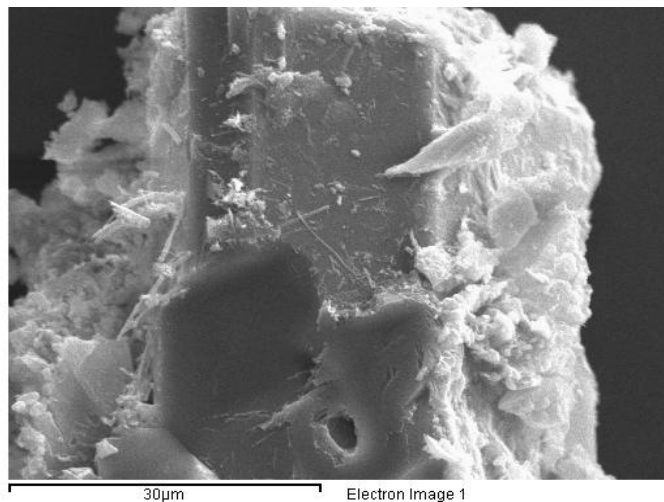
Painted area: 27 x 21 mm

Colour: Green

Munsell No: 5G 5/1



EDX energy spectrum for
SEM-EDAX



A single fractured tabular
crystal set against a large
crystal with a bladed habit in
an otherwise amorphous
assemblage

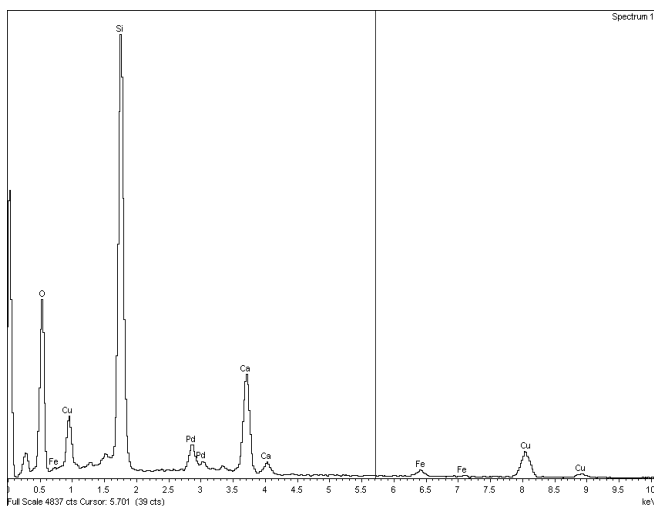
Figure 8.1c HYP08/B



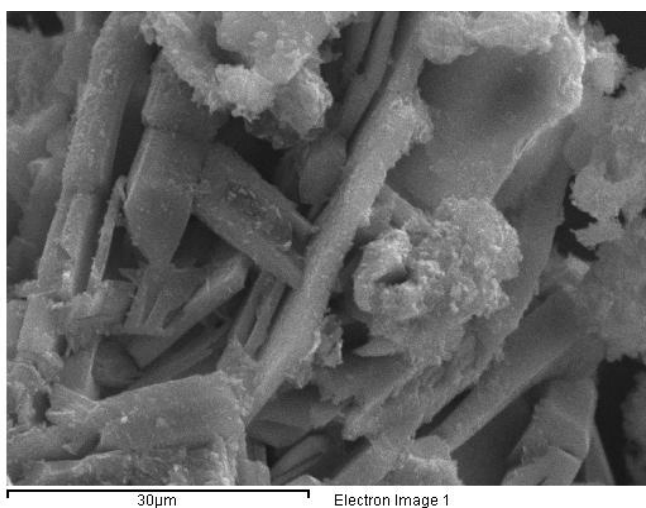
Painted area: 23 x 13 mm

Colour: Dark Green

Munsell No. 5G 8/4



EDX energy spectrum for
SEM-EDAX



Crystal habits are
predominantly acicular
with a few pyramidal
and prismatic forms

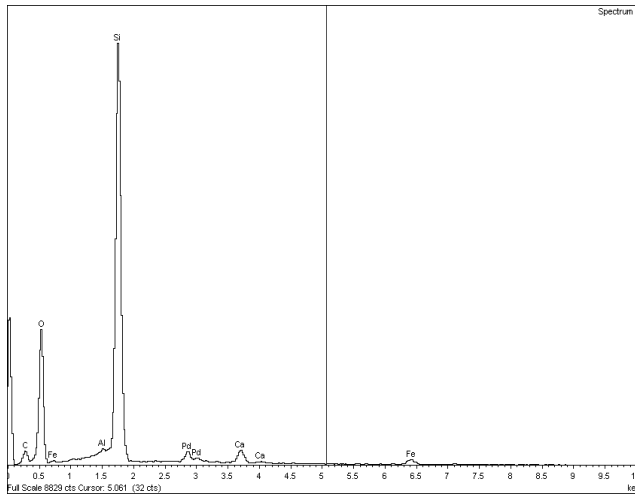
Figure 8.1d HYP08/C



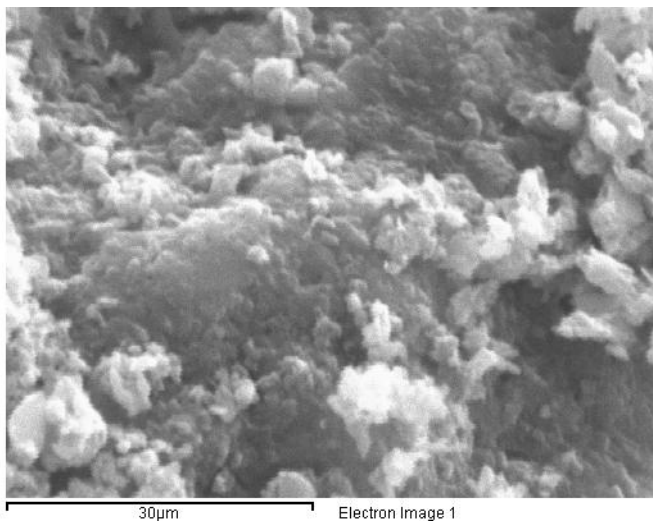
Painted area: 25 x 15 mm

Colour: Blue

Munsell No. 5G 8/1

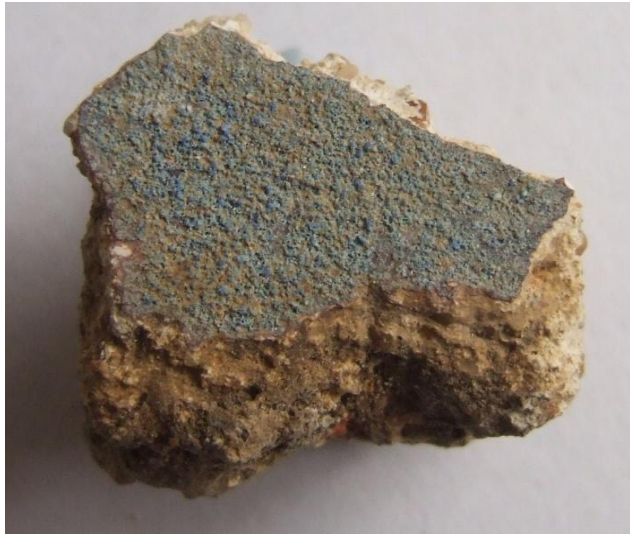


EDX energy spectrum for
SEM-EDAX



An amorphous mass of
crystals with a suggestion
of one or two tabular
habits

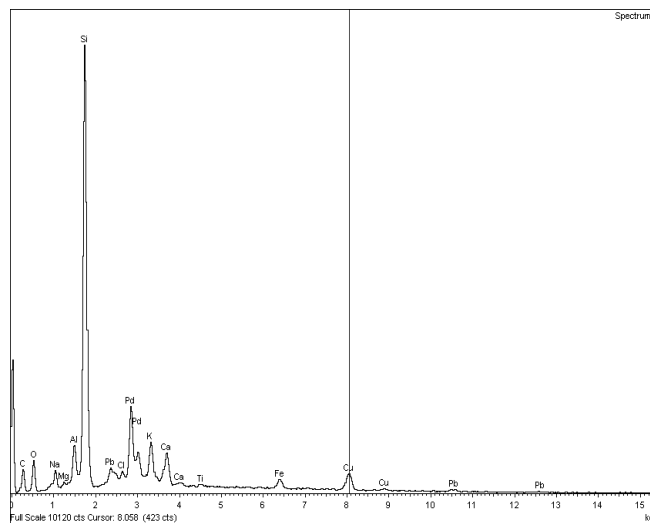
Figure 8.1e HYP08/D



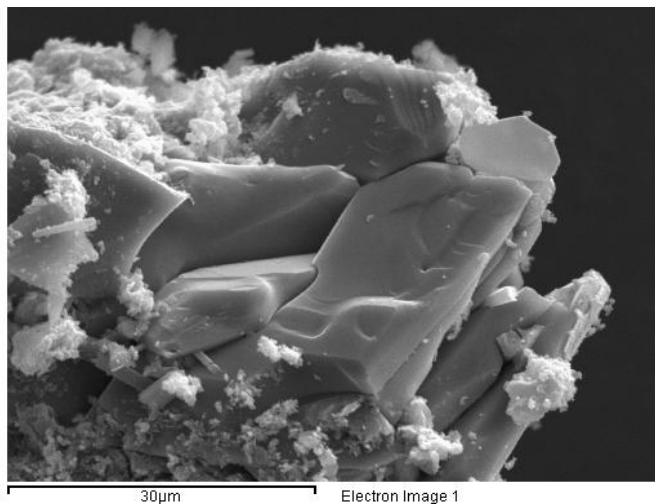
Painted area: 15 x 10mm

Colour: Blue

Munsell No. 10B 8/4



EDX energy spectrum for
SEM-EDAX



Crystals showing tabular and
platy habits with a single
example of a pinacoid face

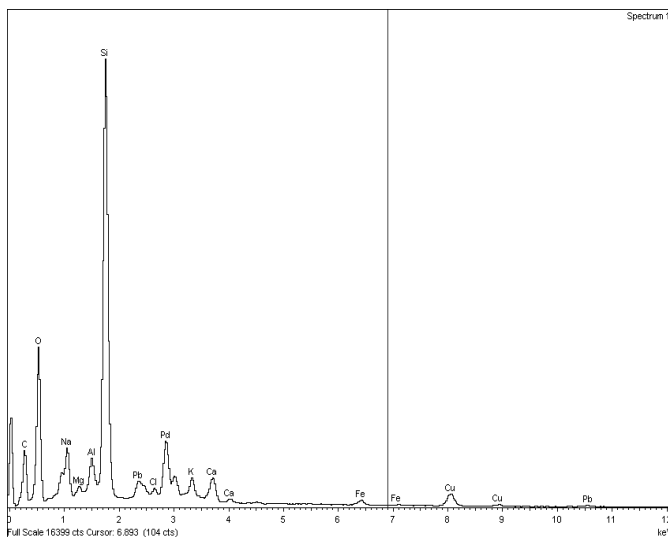
Figure 8.1f HYP08/E



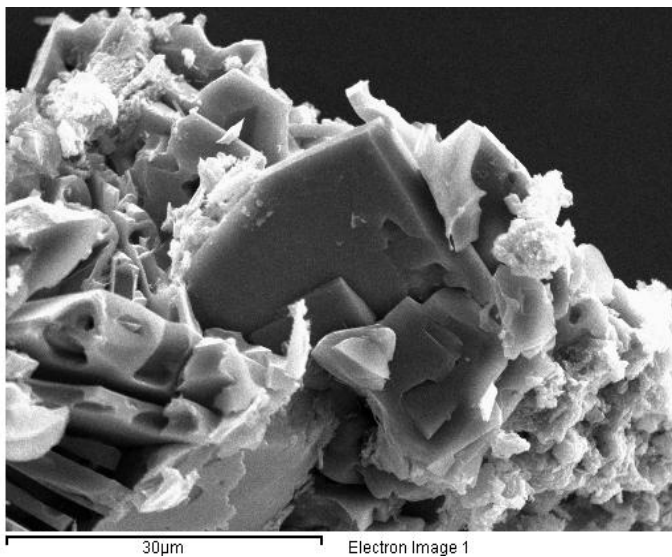
Painted area: 25 x 15 mm

Colour: Blue

Munsell No. 10B 7/4



EDX energy spectrum for SEM-EDAX



A single large tabular crystal with several other crystals showing fractured tabular or platy habits

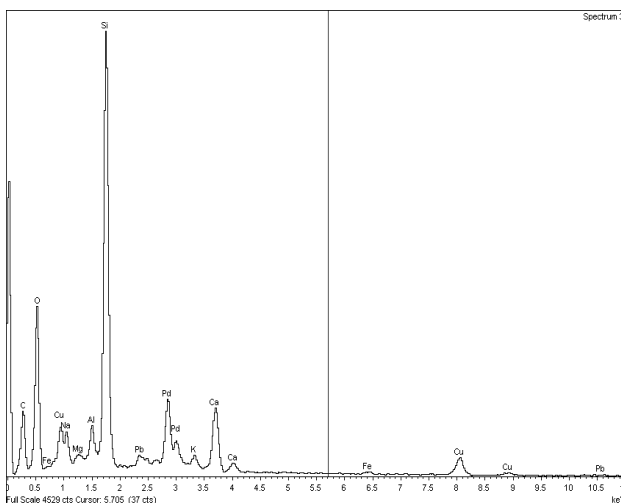
Figure 8.1g HYP08/F



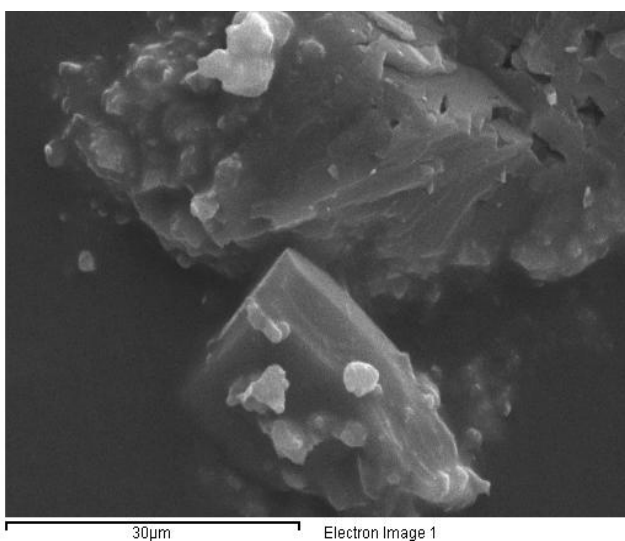
Painted area: 27 x 25 mm

Colour: Dark & Pale Blue

Munsell No. 10B 8/2



EDX energy spectrum for
SEM-EDAX



A single crystal with a
tabular habit and a larger,
fractured crystal with a
cubic habit, together with
scattered fragments

Figure 8.2

Summary of elements detected by SEM-EDAX Analysis of fragments of blue and green painted plaster found at Verulamium Park

| | C | Cu | Fe | Si | Pb | Sn | Na | Ca | Ba | K | Al | Mg | Cl | Ti |
|-----------|---|----|----|----|----|----|----|----|----|---|----|----|----|----|
| HYP08 /06 | x | x | | x | | | | x | | | x | | | |
| HYP08 /A | | x | | x | | | | x | | | | | | |
| HYP08 /B | | x | x | x | | | | x | | | | | | |
| HYP08 /C | x | | x | x | | | | x | | | x | | | |
| HYP08 /D | x | x | x | x | x | | x | x | | x | x | x | x | x |
| HYP08 /E | x | x | x | x | x | | x | x | | x | x | x | x | |
| HYP08 /F | x | x | x | x | x | | x | x | | x | x | x | | |

| | | | | |
|--------------|----|----------|----|-----------|
| KEY : | C | Carbon | Na | Sodium |
| | Cu | Copper | Ca | Calcium |
| | Fe | Iron | Ba | Barium |
| | Si | Silicon | K | Potassium |
| | Pb | Lead | Al | Aluminium |
| | Sn | Tin | Mg | Magnesium |
| | Cl | Chlorine | Ti | Titanium |

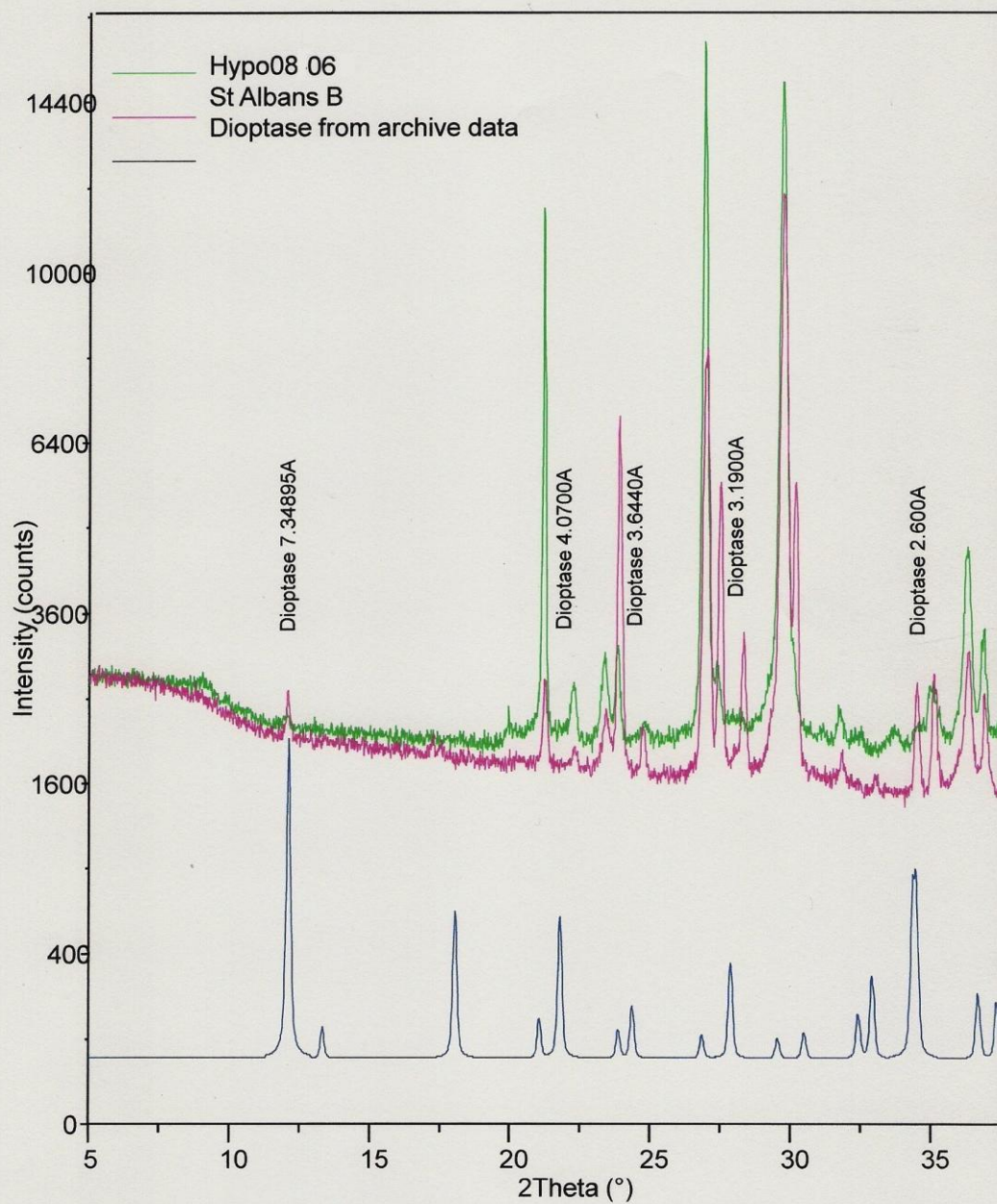
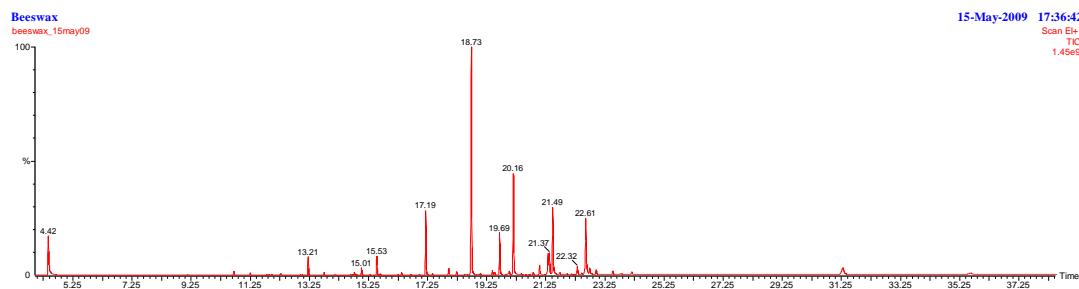


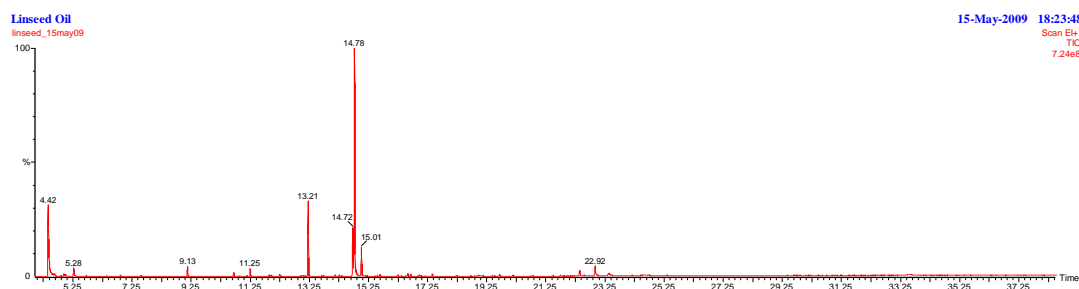
Figure 8. Results from the XRD analysis

Figure 8.4 Results from the GC-MS

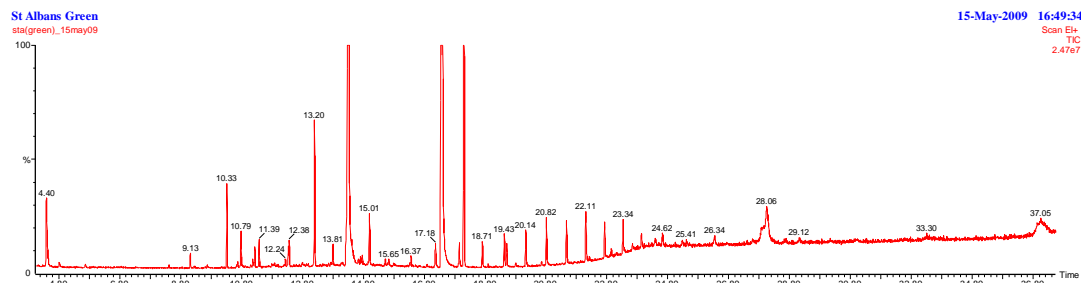
8.4a Linseed oil (21st century)



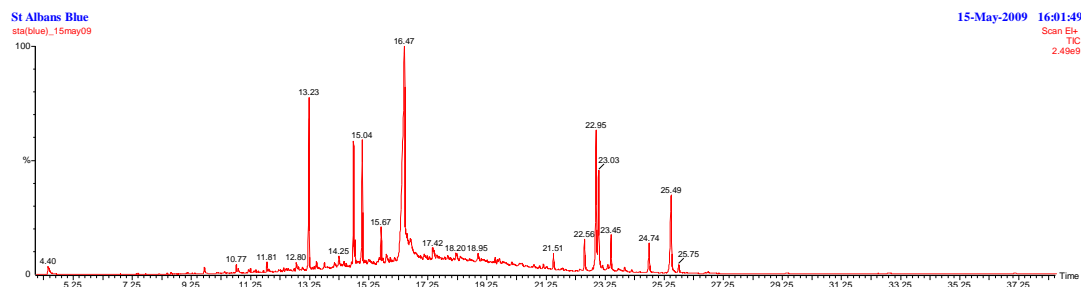
8.4b Beeswax (21st century)



8.4c St. Albans green pigment sample (HYP08/B)



8.4d St. Albans blue pigment sample (HYP08/D)



CHAPTER 9

Experimental Work to Produce Egyptian Blue Pellets

Egyptian blue was the most important blue pigment in antiquity

Chase 1980, 80

9.1 Introduction

In previous Chapters, viz. Chapters 4, 5, 6 and 7 the conclusion drawn from the analytical results was that the ancient artisans did not use a standard recipe for producing Egyptian Blue pellets, but used a variety of ingredients, depending on the materials available at the time.

In their ground-breaking paper of 1914 Laurie, McLintock and Miles described the first modern experiments to reproduce Egyptian Blue pellets. In a set of experiments they adopted Russell's (1895) recipe, using calcium carbonate, copper carbonate, quartz sand together with fusion mixtures and emulated his technique of regrinding and reheating the mixture. The temperature they used varied from 760°C to 890°C and on one occasion reached 1150°C. After experimenting with differing temperatures, Laurie and his co-authors, decided that 850°C was the ideal temperature to produce Egyptian Blue. The firing times that they employed varied from 16 to 20 hours and to 48 hours. In his 1980 paper Chase discussed Laurie's recipe for the production of Egyptian Blue and his own attempts to duplicate the production of Egyptian Blue objects by reducing the firing time to forty five minutes. The outcome of these experiments, he claimed, using the shorter firing time, was a success (see Chapter 2).

The aim of the series of experiments, discussed here, both in the laboratory and under field conditions - when simulated ancient technologies were used - was to determine whether the Egyptian Blue pellets, also known, erroneously, as Pompeian Blue, could indeed be reproducibly manufactured using, firstly, ingredients identified from previously published work and, secondly, simulated ancient technologies. To the best of the author's knowledge, this is the first attempt to reproduce Egyptian Blue pellets using ancient technologies under field conditions. Field experiments were, by their very nature, subject to many uncontrollable factors, unlike those conducted in the laboratory. Additionally, both the laboratory and the field experiments were designed to determine whether, with longer firing periods, the colours of typical Egyptian Blue pellets could be achieved. In all cases the colour of the pellets was identified using the Munsell Book of Color (Matt Finish) 2001 and the pellets were further examined microscopically to determine their surface structure so that comparisons could be made with pellets found on archaeological sites.

The ingredients used in the present series of experiments were identical to those used by Russell (1895), Laurie and colleagues (1914) and corresponded to those of Chase's second formula (1980). The recipe used for these experiments (with one exception) consisted of: silica, 64.6g, copper carbonate 15.4g, calcium carbonate, (Na_2CO_3 , natrite) 12.4g and, as the flux, sodium carbonate, 7.2g *ie* in the ratio of 4.2 : 1 : 0.8 (and 0.5 for the flux). Although the actual volumes of ingredients used might vary, depending on the number of pellets to be formulated, they were always employed using the above ratio.

In addition to testing the established recipe, the author's laboratory experiments systematically examined the effects of changing and extending the firing times and conditions. These modifications are shown on the flowchart (figure 9.1). Further experiments based on the findings outlined in previous Chapters and with consideration of the materials which would have been available to ancient

artisans led the author to *also* make the following modifications, *viz.* the use of copper filings, ground malachite and rock chalk.

9.2 Laboratory based experiments

In the first experiment, the ingredients were mixed together with a small amount of water (Bianchetti *et al.*, 2000). Nine pellets were made and allowed to dry naturally (Figure 9.2 shows Egyptian Blue pellets before firing). After drying the pellets were placed in a ceramic pot and then inserted into a Muffle furnace for forty-five minutes at 850°C under aerobic conditions. The pellets were removed from the oven after 45 minutes and, when cooled, were examined with a fibre-optic microscope (Niotic SMZ 168-Photonic PL 3000). Clusters of blue/green crystals had formed on the outside of all the pellets. When sectioned the inner surface appeared to be very dark in colour possibly due to oxidation of the copper to copper oxide (CuO).

In a second experiment one of the nine pellets was re-ground and re-fired at the same temperature for 45 minutes and then again examined under the fibre optic microscope. This pellet was itself then reground and on examination the colour of the ground pellet was found to be more grey than blue (Munsell No. 5PB 6/2) see figure 9.3. In a third experiment that particular pellet was then reformulated by adding a small quantity of water and allowed to dry naturally. It was re-fired for a period of one hour, the temperature of the oven remaining constant at 850°C. On macroscopic examination the texture and colour of the pellet had not changed from that achieved after the previous firing, *ie* it did not change its colour after 3 firings - over a total of 2½ hours.

The remaining eight pellets were also re-ground, reformulated and allowed to dry naturally. In the fourth experiment they were re-fired for one hour at the same temperature, *ie* these pellets were fired twice for a total period of 1¾

hours. On examination it was noted that the pellets had become more blue/green in colour (Munsell No. 10B 3/4) than the initial pellet (whose colour had not changed over its three firings). There appears to be no obvious explanation for the difference in the final colour of these eight pellets as compared with the single re-fired pellet. However, on reflection it was considered that the use of grains of sand of different size might offer a possible explanation since all the other ingredients (*viz.* the copper, calcium and sodium bicarbonate) were ground to the same fine consistency.

Vitruvius (1960) notes that the elements of the mixture used to form the pellets should be ... *brayed together so finely that the product is like a meal* ... (Book VII, 218:1). In the previous experiment very fine, unsieved, sand had been employed. It was decided, therefore, that the sand should be passed through a very fine archaeological sieve (mesh size 0.355 mm) thereby removing larger particles. It was subsequently ground to produce a consistence resembling that of fine baking flour. In the fifth experiment a combination of the sieved and ground sand with the other (powdered) ingredients produced a more pliable mixture. The formulation of a further nine pellets became an easier process. After drying the pellets were placed in the oven for a period of five hours, the temperature remaining at 850°C. Once cooled the pellets were examined and the colour of the ground pellet was noted to vary from a dark blue to a dark grey (Munsell No. 10B 5/4) but not the traditional colour associated with Egyptian Blue. Figure 9.4 shows one of these pellets with a grey/blue coloration.

In a sixth experiment the standard recipe, with the sieved and ground sand, was again used and eight pellets were fired for twenty-four hours. The temperature remained at 850°C. Once cooled the pellets were examined by naked eye and then studied under the fibre-optic microscope. The change in colour was quite remarkable. They were consistently a dark blue in colour (Munsell No. 5PB 4/8), figure 9.5.

Once cooled these eight pellets were re-fired for a further 24 hours to see if they would change colour yet again: four of these pellets were finely re-ground and the remainder four were coarsely re-ground. After this second-twenty hour firing the colour had again changed dramatically: the finely ground pellets were cobalt blue in colour (Munsell No. 5PB 5/8) and the coarsely ground pellets were a royal blue in colour (Munsell No. 10B 4/8). Vitruvius explained this change when he said: *As soon as the copper and sand grow hot and unite under the intensity of the fire, they mutually receive each other's sweat, relinquishing their peculiar qualities, and having lost their properties through the intensity of the fire, they are reduced to a blue colour* (idem.).

In the eighth experiment the length the firing time was increased to a total of ninety-six hours using the same recipe, with the sieved and ground sand. The remaining ingredients were added and eighteen pellets fired for an initial forty-eight hours. After cooling, the pellets were re-ground and re-fired for a further 48 hours, following which the colour had changed to a vivid blue (Munsell No. 5PB 4/8), similar to the colour of traditional Egyptian blue.

Following the above two firings, in the ninth experiment, nine of these pellets were again re-ground and then re-fired at 850°C for a further 48 hours (giving a total firing time of 144 hours). Once cooled these nine pellets were seen to be a dark blue in colour (Munsell No. 5B 10/4), figure 9.6. There was a distinct similarity in colour to one of the first or second century AD pellets (FBE02 1071/1741a) found in red clay that had sealed an early ditch, during the 2002 excavation season at Fishbourne Roman Palace, Chichester, (Clegg, 2005, 78).

From the above series of experiments it was clear that Egyptian Blue had been successfully produced. Under experimental conditions, of three firings and two episodes of regrinding, it took a total firing time of 144 hours to produce a pellet

(one of the nine of experiment nine) whose colour was more-or-less indistinguishable from that of the Fishbourne Roman Palace pellet, FBE02 1071/1741a, (figure 9.7). Both pellets, with almost identical colours, were examined with a fibro-optic microscope and it was seen that the structure of the Fishbourne pellet, although fibrous to touch, looked as though it had been coarsely ground, whereas the pellet produced for this study showed a much finer texture.

In order to obtain the brilliant blue associated with Egyptian Blue found in ancient specimens (both pellets and applied pigment) the laboratory-based experiments indicated that the ingredients had to be finely ground and that the firing time, which clearly also influenced the colour obtained, needed to extend over a period longer than a few hours. These results clearly contradict the statement by Chase (page 37, above) in which he claimed to be able to produce Egyptian Blue with a firing time of only 45 minutes.

As a single ‘one off’ study it was decided to continue with an experiment – in the laboratory – using ingredients similar to those that may have been used by the ancient Romano-British craftsmen: copper filings were used instead of copper carbonate, chalk (obtained in this case from Beachy Head in Eastbourne, Sussex) and a local fine beach sand used as a source of silica. Pellets made from these ingredients were fired for twenty-four hours at 850°C. Regrettably this experiment failed as a result of a power cut during the firing period.

A second ‘one off’ experiment was conducted to determine whether there would be any variation in the colour of the pellets if ground malachite was substituted for copper carbonate or copper filings, the other ingredients remaining unchanged. Eight pellets were fired for forty-eight hours, the temperature remaining at 850°C. On completion the colour appeared to be more green/blue (Munsell No.10B 4/6) than just a plain blue, as shown in figure 9.8. These eight

pellets were again re-ground and re-fired for a further 48 hours to see if the colour would change; however the colour remained unchanged, showing the same green/blue hue.

From the original nine experiments eight pellets were selected for further study. Two pellets were selected from each of the following experiments: experiments one, five, six and nine. One pellet from each of these experiments was macerated and examined using SEM-EDAX to determine its crystal structure. The remaining four pellets, whose colour had been recorded, were finely ground, mixed into a paste, using water and applied to squares of damp lime mortar (4 x 4 cm) in order to ascertain what colour the pigment would produce when used as a paint. The colour of the ground pellet, a description of the crystal habit and the colour of the applied pigment is shown in figure 9.9a to 9.9d.

It is possible to correlate the crystal habit of the four pellets that formed this twelfth (and final) laboratory experiment, just described, with their firing times because the production history of these pellets (the firing time, degree of grinding, the specific ingredients, etc.) is meticulously recorded. Although some archaeological specimens may demonstrate a crystal habit similar to that of these four pellets it is not possible to thus conclude any information about their production history – the number of possible variables is totally unknown.

9.3 Field trials using ancient technology

After the successful production of Egyptian Blue pellets, under controlled laboratory conditions, it was considered that similar experiments, carried out using simulated ancient technologies, under field conditions, would prove invaluable in understanding the knowledge skills of the ancient artisans. The kilns used in these experiments were a simulated Bronze Age Clamp Kiln and a simulated Iron Age Belgic Kiln. While there is no direct archaeological

evidence to suggest that clamp kilns were used in the production of Egyptian Blue it should be noted that such structures are unlikely to be well preserved in the archaeological record, due to the very nature of their construction and use – a shallow pit containing the remnants of charcoal and burnt earth soon disappears into the ever-changing landscape.

The Belgic kiln may have been used by the Roman craftsmen during the first and second centuries AD. Evidence of the existence of workshops (for instance for metal working and for potters) has been found at Fishbourne Roman Palace in Chichester, at Turners Hall Farm, near St Albans and at Piddington Roman Villa in Northampton. This suggests the possibility that kilns may have been used in the production of various commodities associated with the site. Whether those kilns were similar in construction to the simulated Belgic kiln used in these experiments is debatable, although the general construction and firing conditions of the simulated kilns are thought to be representative of Romano-British era technology.

In 2006 Tristan Bareham, Chief Executive of Sussex Archaeological Society, and Ian Dunford of East Sussex Archaeology and Museum Projects, who specialize in firing pots using kilns of Bronze and Iron Age construction, agreed to assist. Over a three year period experiments took place at the annual week long Ancient Crafts and Technology Summer School at Michelham Priory, which is owned by Sussex Archaeology Society, Upper Dicker in East Sussex and also at a single Wood Craft Fair at Bentley Wildfowl Trust, near Ringmer, East Sussex.

9.3.1 Bronze Age Clamp Kiln

Several experiments were conducted. Pellets were made, using the refined recipe in a single large batch and divided into lots for use in each of the

following investigations. In the first experiment a reconstructed Bronze Age Clamp Kiln was used (figure 9.10). A shallow pit was made in the ground in which hot charcoal was placed. The charcoal was covered with large pieces of dried local wood from native species such as ash, oak, hornbeam and elder in the form of a raft weighing twelve kilograms. The pellets were placed in three small pre-fired pots, made from local sand and clay, and left uncovered within the kiln. They were placed in different positions on the base of the raft (figure 9.11) where the intensity of the fire would partially oxidise the pellets over the firing period. The raft was then covered, in the shape of a tepee, by 'rods' of local wood which itself was enveloped with strips of turf, see figure 9.12 (a) and (b). A digital pyrometer was inserted into the clamp kiln every twenty minutes to record the rising temperature which, after a period of five to six hours, eventually reached 800°C. The intention was to maintain this temperature for up to ten hours. The clamp kiln was left to burn overnight. Figure 9.13 shows the kiln during the period of firing. The remains of the kiln were uncovered after a time lapse of twenty-four hours and the pots left to cool, figure 9.14.

After a cooling period of several hours the pellets were closely examined. The pellets in one of the pots had started to turn blue (figure 9.15) which suggests that these pellets were exposed to a higher temperature and Egyptian Blue had begun to form. The pellets in the other two pots had turned black in colour. The black colour is most probably due to copper oxide formed by decomposition of copper carbonate.

Using a second batch of pellets the same experiment was repeated the following day. It was decided to make the pit slightly deeper and to increase the amount of dried wood with the anticipation that the clamp kiln would reach a temperature of at least 800 °C and that this temperature would be sustained for more than ten hours. The pellets were divided equally into three different pots.

Again temperature readings were recorded, at regular intervals, using a digital pyrometer. The kiln was left to burn for twenty-four hours. On the following day when opening the clamp kiln, to allow the pots could cool, it was noted that the internal structure of the kiln was glowing red hot. It was surmised that the internal temperature must have reached, much to everyone's surprise, overnight, figures well in excess of 1000°C. The pellets were black in colour, figure 9.16.

In a final experiment twenty-eight kilograms of wood was used in an attempt to encourage the kiln to sustain a temperature of 800°C over a longer period of time, possibly up to twelve hours or more. Again, as with the first two experiments, the temperature was monitored at regular intervals and after a period of four hours the temperature had risen to 488°C. The temperature continued to be monitored until it reached 800°C. Unfortunately this experiment did not succeed: during the night it became very windy and by early next morning the clamp kiln had completely burnt out. The pellets had started to form a agglomerate (figure 9.17) but with effort, once cooled, they were separated (figure 9.18) and returned to the laboratory to be studied under fibre optic microscopy. On examining the pellets it was seen that the ingredients had started to fuse together, figure 9.19.

9.3.2 Iron Age Belgic Kiln

The next experiment took place at Bentley Wildfowl Trust where a reconstructed Iron Age Belgic Kiln (figure 9.20) was employed. A further batch of pellets were made using the standard recipe. The lower part of the Belgic kiln was constructed of a clay-lined turf wall. Inside the kiln was a pre-fired clay pedestal upon which pre-fired clay bars were placed. For this experiment two uncovered pre-fired pots containing the pellets were placed in the middle of a group of fifty-five pots ready for firing (figure 9.21), the latter being stacked

upside down. The upper half of the kiln was then covered with layers of turf and clay to form a chimney. Local dried wood was lit in front of the fire box and hot embers were gradually fed into the kiln, figure 9.22, great care being taken not to dislodge the central pedestal. A digital pyrometer was placed half way up the kiln and the temperature was recorded every twenty minutes. It was observed that the temperature rose evenly at about 100°C per hour. After some eight hours the temperature finally reached 883°C and remained so for about two and a half hours. The kiln was left to cool overnight. During the following morning, when it had cooled sufficiently, the upper part of the Belgic kiln was partially dismantled (figure 9.23) thus exposing the fired pots including, the two pots containing pellets, figure 9.24. The colour of the pellets had partially changed to a slightly blue colour as can be seen in figure 9.25. Under microscopic examination one of the pellets clearly shows that some of the components had indeed turned to a blue coloration, figure 9.26. The experiment could thus be described as being at least partially successful.

9.4 Discussion

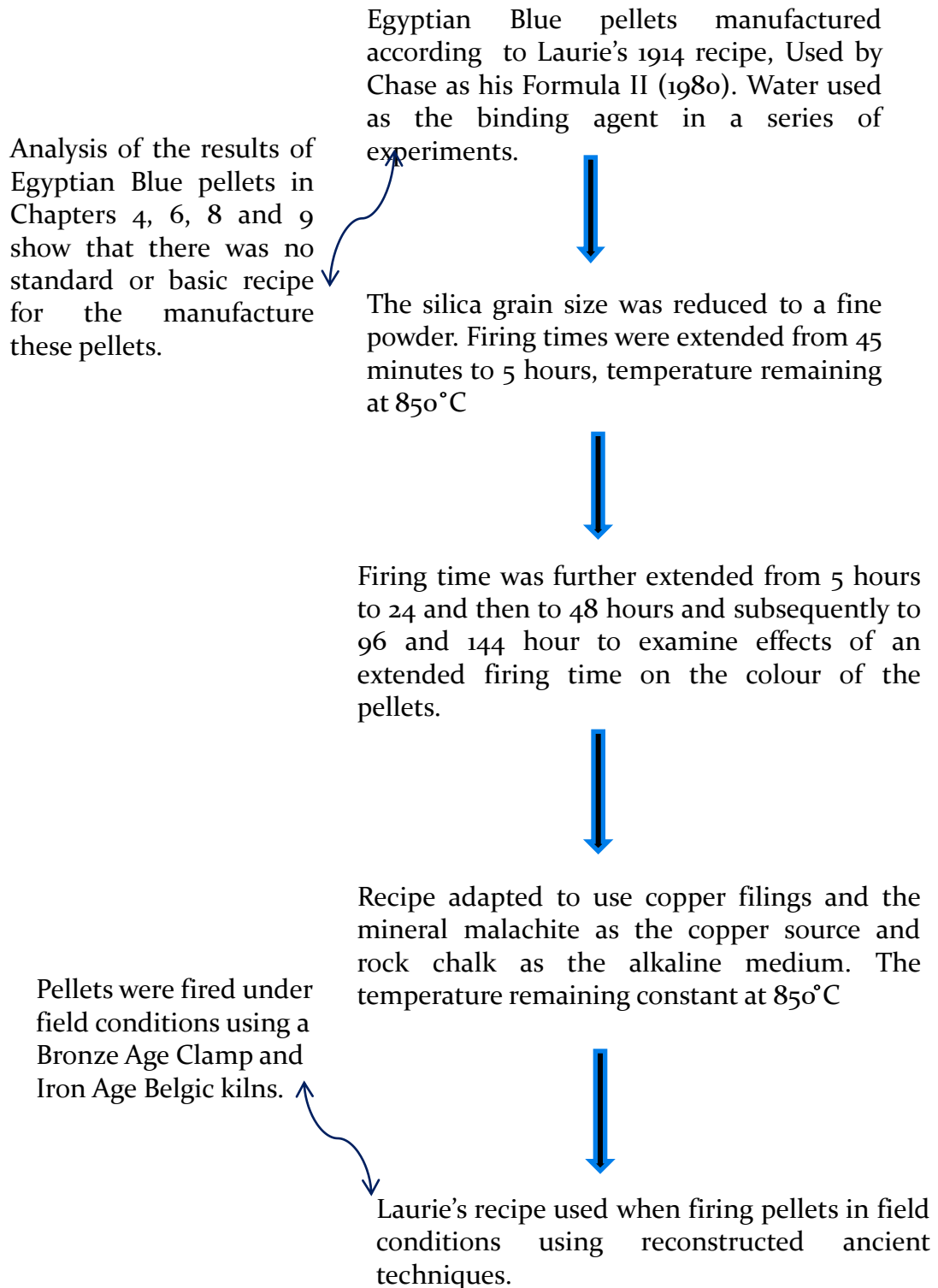
In the series of nine laboratory experiments it was clearly demonstrated that the recipe and firing times are of crucial importance in the production of Egyptian Blue pellets. This confirms the findings of Russell (1895) and Laurie *et al.* (1914). Dr Russell, who examined samples of Egyptian Blue from Flinders Petrie's sites at the Egyptian towns of Kahun and Gurob and undertook his own experiments to produce the pigment, wrote in his notebooks ... *In the case of the samples containing calcium carbonate [it was] found that in every instance they had been ground and reheated sometimes several times before the blue was properly developed, the sample after the first heating very often being black, [and] the blue gradually improving with each new heating.* (quoted in Laurie, *et*

al. 1914, 421). This statements, like the findings presented above, are (as already suggested) in marked contrast to the claims of Chase (1980).

The failure of the field experiments to produce the brilliant blue normally associated with Egyptian Blue confirms that it is important to maintain the temperature of 850°C over a period of time, probably greater than 48 hours. It is simply not known for how long the kilns were fired nor how the Roman artisans ‘controlled’ the temperatures of these kilns. Vitruvius noticeably fails to mention these two factors. It is not known whether the artisans who decorated the interior walls of houses and villas for the wealthy carried stocks of Egyptian Blue pellets as they moved from one site to another or whether they used local basic clamp kilns for the manufacture small quantities of ‘as required’ Egyptian Blue pellets.

There is, at present, no archaeological evidence to suggest that the manufacture of Egyptian Blue pellets in Roman Britain was carried out on a scale large enough to be described as “factory” produced that would have necessitated the use of Egyptian fritting-pans. During the early period of the Roman occupation of Britain it is possible that kilns, similar to Belgic kilns, had a multi-purpose function, including the manufacture of Egyptian Blue pellets. For simple economic reasons it may be considered unlikely that these Belgic-style kilns were used for the sole purpose of producing Egyptian Blue pellets. The various apparent successes and failures demonstrated by the these field studies, using simulated ancient technologies, clearly indicate that further field work is required in order to re-produce the blue colour obtained by the Roman or Romano-British artists in the production of Egyptian Blue in Romano-Britain.

Figure 9.1 Flow chart for the preproduction of 21st Century Egyptian Blue pellets



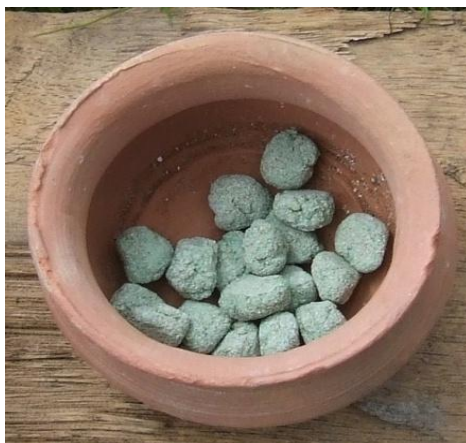


Figure 9.2 Unfired Egyptian Blue pellets

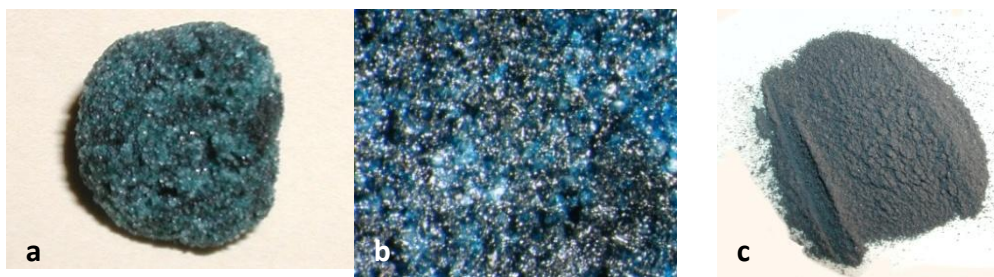


Figure 9.3 (a) pellet fired for 90 minutes, experiment 2. (b) examined under microscope x 20. (c) ground pellet, Munsell No. 5PB 6/2.

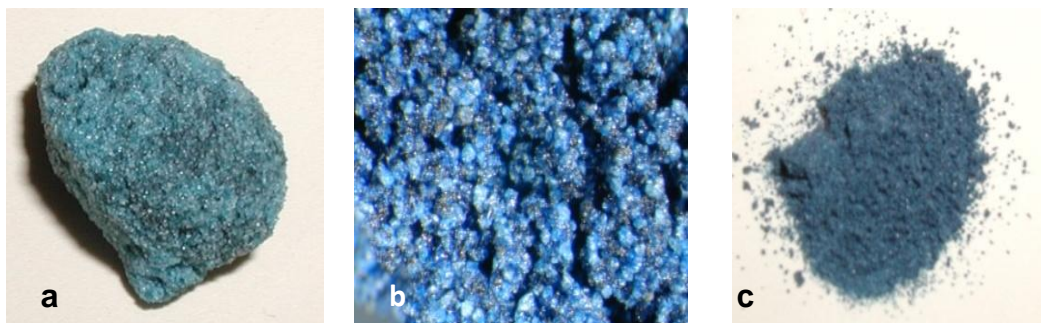


Figure 9.4 (a) pellet fired for 5 hours, experiment 5. (b) examined under microscope x 20. (c) ground pellet, Munsell No. 10B 5/4.

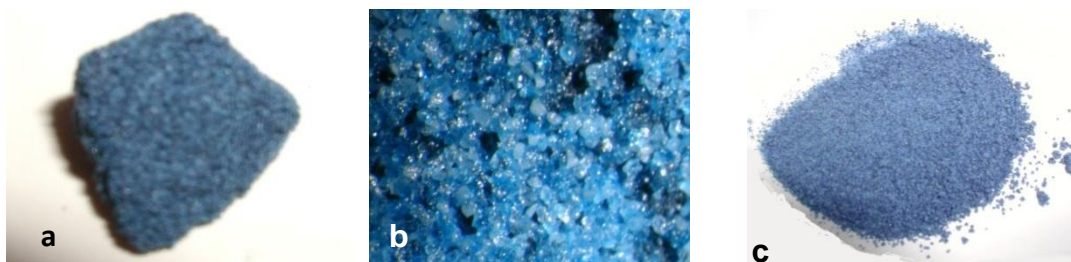


Figure 9.5 (a) pellet fired for 24 hours, experiment 6. (b) examined under microscope x 20. (c) ground pellet, Munsell No 5PB 4/8.

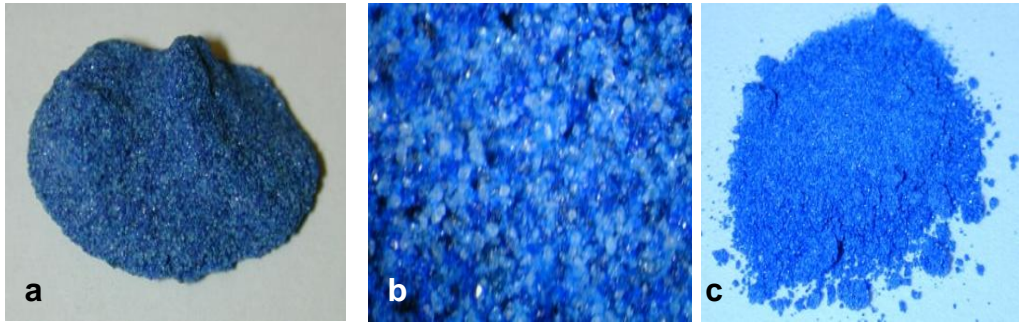


Figure 9.6 (a) pellet fired for a total of 144 hours, experiment 9. (b) examined under microscope x 20. (c) ground pellet, Munsell No 5B 10/4. The colour is similar to that, shown below, found during the Fishbourne Roman Palace 2002 excavations.



Figure 9.7 FB02 1071/17421a, Munsell No.5PB 5/8.

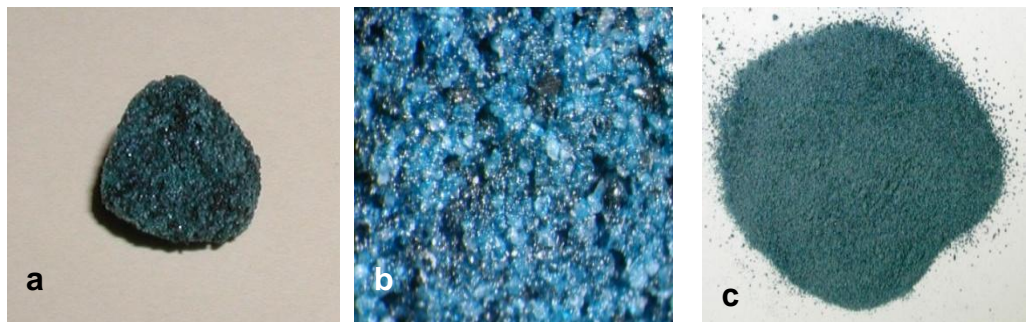
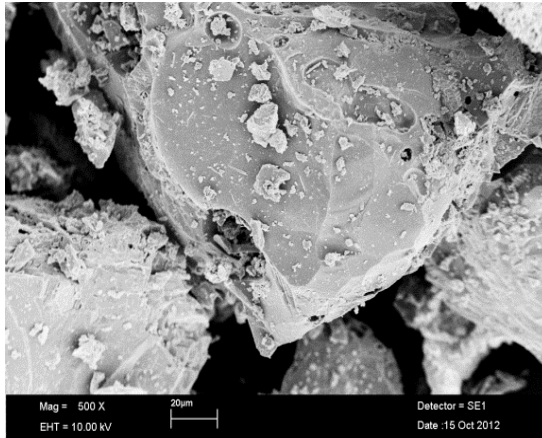


Figure 9.8 (a) Malachite pellet fired for 48 hours, second 'one off' experiment. (b) examined under microscope x 20. (c) ground pellet, Munsell No 10B 4/6.

Figure 9.9a Ground pellet, crystal habit and the colour of applied pigment



Ground pellet fired for 90 minutes, experiment 2.



A single large crystal with tabular habit and other fractured forms.

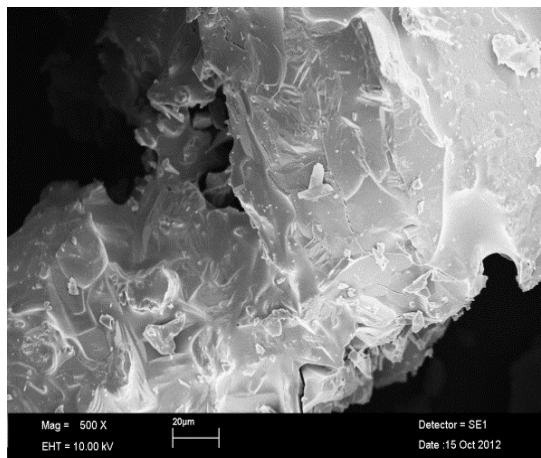


The ground pigment as applied to lime mortar, Munsell No.10B 7/2.

Figure 9.9b Ground pellet, crystal habit and the colour of applied pigment



Ground pellet fired for 5 hours, experiment 5.



A single large crystal with unidentifiable habit.

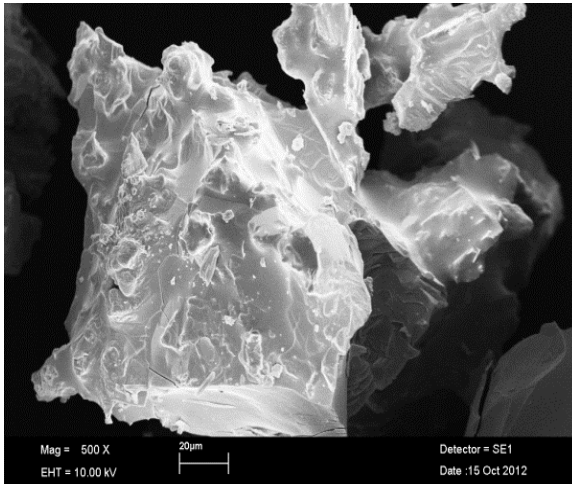


The ground pigment as applied to lime mortar, Munsell No. 5PB 8/4.

Figure 9.9c Ground pellet, crystal habit and the colour of applied pigment



Colour of ground pellet fired for 24 hours, experiment 6.



A large fractured crystal with cubic habit and other fragments

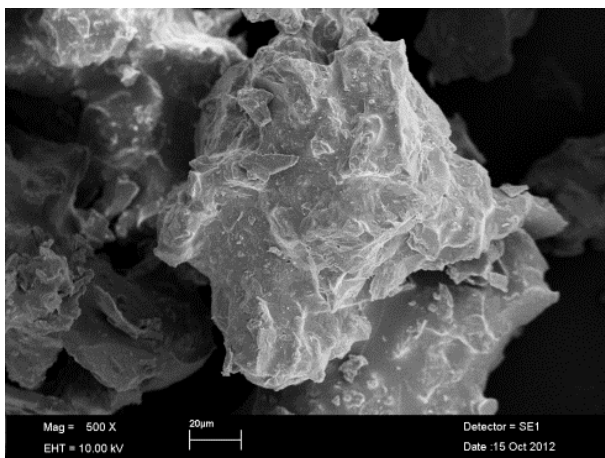


The ground pigment as applied to lime mortar, Munsell No. 10B 7/4.

Figure 9.9d Ground pellet, crystal habit and the colour of applied pigment



Colour of ground pellet fired for 144 hours, experiment 9.



Several large crystals with fractured cubic habits



The ground pigment as applied to lime mortar, Munsell No. 5PB 6/8. Unlike other examples this shows a noticeable sheen.

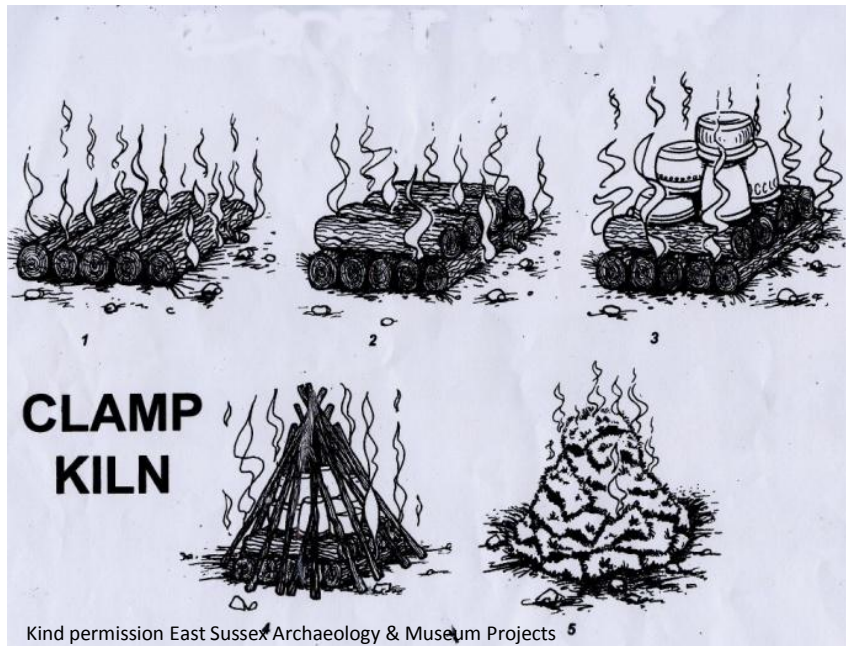


Figure 9.10 A drawing of a re-constructed Bronze Age Clamp Kiln



Figure 9.11 Raft made with local wood, pots placed on base of raft.



Figure 9.12(a) Showing 'rods' of local wood



Figure 9.12(b) Enveloped in strips of turf



Figure 9.13 Clamp kiln was left to burn overnight.



Figure 9.14 Clamp kiln uncovered, pots left to cool. Yellow arrow shows position of the digital pyrometer.



Figure 9.15 Showing the pellets that had started to turn blue, first experiment



Figure 9.16 Results from second experiment. The pellets were black in colour.



Figure: 9.17 Failed experiment: pot showing the ingredients having fused together.

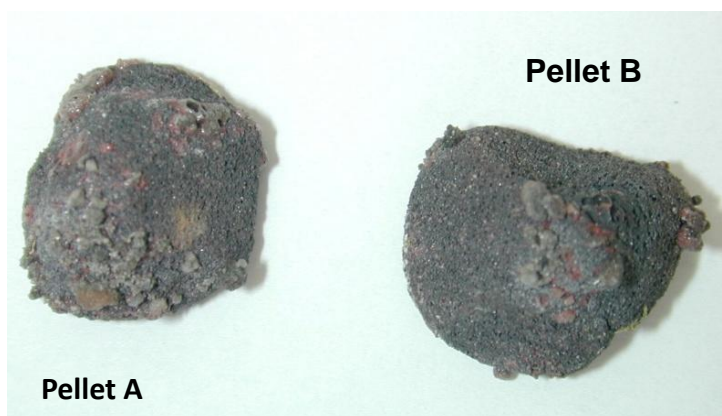


Figure 9.18 Separated fused ingredients, Pellet A and B.

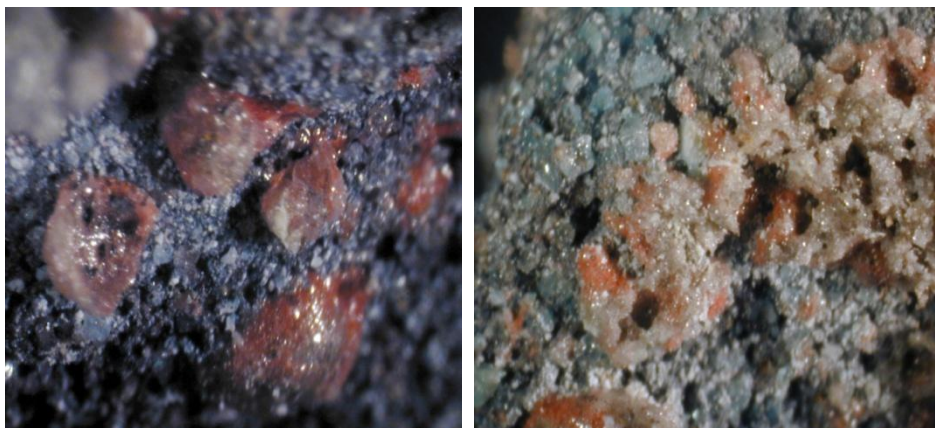


Figure 9.19 Pellets A and B examined under the microscope x 20

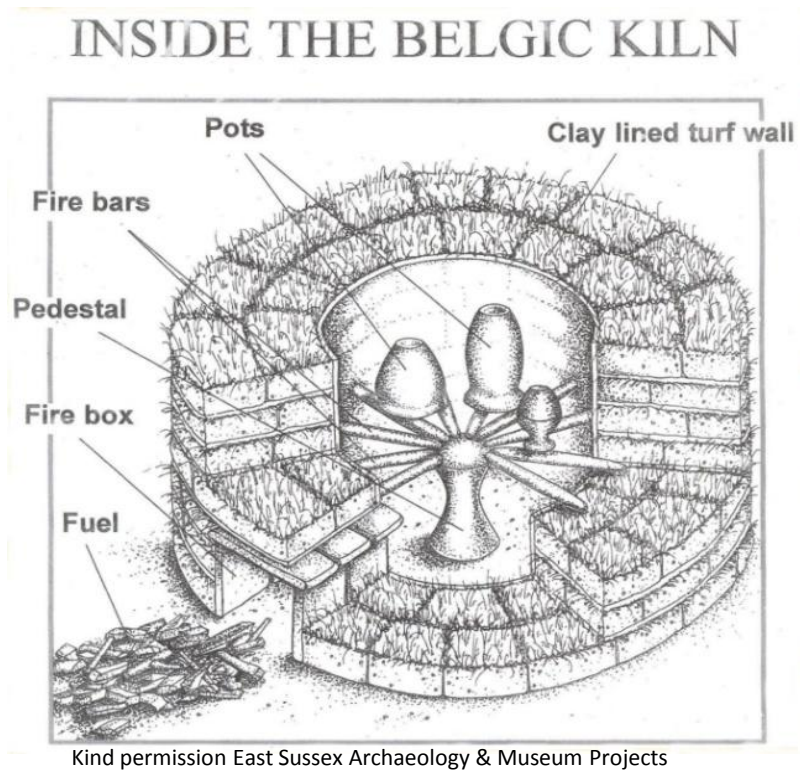


Figure 9.20 Drawing of a re-construction of a Belgic Kiln



Figure 9.21 The yellow arrows show 'raw' Egyptian Blue pellets ready for firing



Figure 9.22 The author feeding the hot embers into the kiln's fire box



Figure 9.23 The uncovered kiln being left to cool



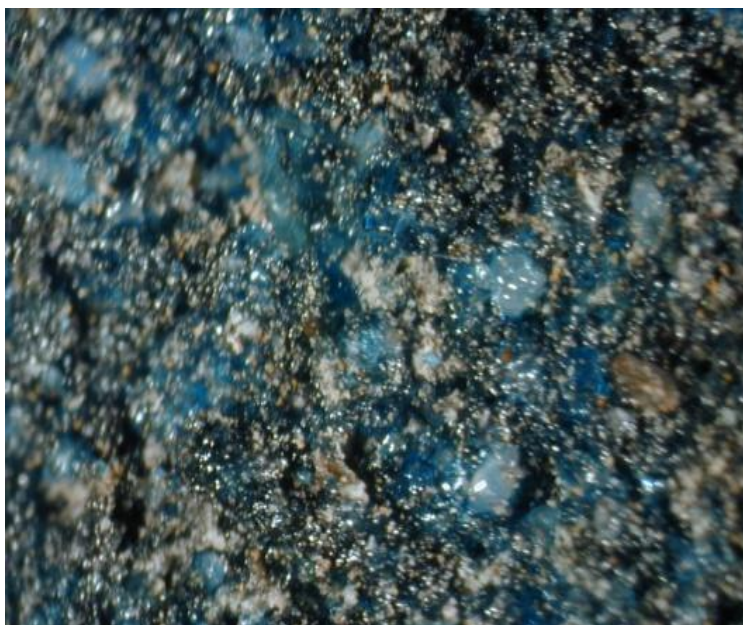
Figure 9.24 A view of the pellets cooling in the Belgic Kiln



Figure 9.25 Showing the pellets having partially changed to a blue colour



Figure 9.26 One of the pellets removed from the pot (figure 9.25) Munsell No. 10B 3/6, shown below magnified x 20



CHAPTER 10

Conclusion

*... colour is more stimulating than line-drawing, because it is life-like
... and gives more satisfaction*

Plutarch 1st century AD
(quoted in: *Colour and Culture* by J Gage, 2001, 15)

10.1 Considerations

After an extended examination of published papers and following consideration of the various geochemical and analytical methods used in archaeological research it was decided to use, where appropriate, LA-ICP-MS, SEM-EDAX, XRD, GC-MS and micro-Raman Laser Spectroscopy as the analytical methods most appropriate for the investigation of the Egyptian Blue pellets and fragments of blue and green painted wall plaster available for this study. It is understood that this is the first in-depth study of Egyptian Blue pellets used in Romano-British wall plaster paintings to be undertaken using both LA-ICP-MS and SEM-EDAX analytical techniques.

When examining archaeological specimens or artefacts it is evidently important to consider, where possible, the method of construction, the raw materials used (and also their source), as well as noting any restoration work that might have been undertaken. It is, furthermore, advisable to determine, where practicable, the major and minor elements, also the trace elements found in the manufactured specimen or artefact. Different investigative techniques will prove better than others for different artefacts. Some techniques will be inappropriate for certain

exhibits. In many instances it is not possible to remove even the smallest of samples from the original artefact. This will clearly limit the tools available for the investigation of that particular specimen.

A previous study demonstrated the value of XRF in determining the presence of lead (Relative Atomic Mass, RAM, 207.2) and lighter elements in the Egyptian Blue pellets found in the 1997, 1998 and 1999 excavations at Fishbourne Roman Palace (Clegg & Freeman, 2003). At the time that this present study was planned XFR was unavailable at Sussex University. However, the new and more 'high tech' facility of LA-ICP-MS was available and this, combined with the well established SEM-EDAX technology, was considered to provide enough analytical power to commence this investigation.

The application of LA-ICP-MS technology to the twelve Egyptian Blue pellets found in the 2002 excavation at Fishbourne Roman Palace demonstrated the presence of many relatively abundant elements, all of whose RAM was lighter than that of lead, including tin, iron and copper. Silica, as a major element was identified in nine of the twelve pellets (see figure 4.4A, page 99). It is recognized that LA-ICP-MS technology was unable to detect the presence of many trace elements in this study. In contrast to this the SEM-EDAX was able to identify, among the relatively abundant elements, silica, aluminium, magnesium, copper, iron and calcium (RAM, 40.08). This technique was also able to detect a large number of trace elements including titanium, magnesium, potassium and sodium. However, it is evident from figures 4.4A and 4.4B that the SEM-EDAX technology was unable to detect the presence of lead and tin which was identified by the LA-ICP-MS technology.

The above results suggest that the SEM-EDAX analysis is in general more efficacious in identifying trace elements in the Egyptian Blue pellets than the LA-ICP-MS technology. This is the case for all of the sites with the exception of Piddington where the different analytical methods both identify a different range of trace elements, although the SEM-EDAX technology was again unable (at Piddington) to detect lead and tin in the majority of the pellets.

From the investigations it is also apparent that these two analytical methods identify different elements, even when it is the major and minor elemental composition that is being analysed. Thus it is clear that neither LA-ICP-MS technology nor SEM-EDAX analyses alone have given a clear picture of the elemental composition of the Egyptian Blue pellets used in this study. All of these pellets, with the exception of those from Verulamium, were found in a soil matrix, and were subjected to weathering and degradation, and this fact has been a major factor in the determination of their elemental composition. It is known, for instance, that water will, over time, leach out alkali and some elements, such as potassium and sodium, from the pellets.

According to Kuisma-Kursula (1999) SEM-EDAX is known to have a poor sensitivity to trace elements (see Chapter 3, page 64). However, the data presented in this study of the pigments used in the Egyptian Blue pellets found on Romano-British sites suggests the contrary: SEM-EDAX was able to identify a large range of trace elements in the Egyptian Blue pellets available for analysis.

The marked difference in the isolation and identification of elements by the two techniques (LA-ICP-MS and SEM-EDAX) represents the differing

susceptibility of the analytical tools to the quantities of the elements in the samples presented for analysis. A further complicating factor regarding calcium detection by LA-ICP-MS is that the signal from the main isotope (^{40}Ca) suffers major interference from the Argon 40 isotope gas used in the analysis. Consequently, the detection of calcium in the samples relies on identification of ^{42}Ca , ^{43}Ca , ^{44}Ca , ^{46}Ca and ^{48}Ca isotopes, all of which have very low natural abundance. Furthermore, the Sussex University LA-ICP-MS machine, dating from the early 2000s, is unable to compete with more recent machines which are able to analyse data in much greater detail. However, it may be considered that a judicious combination of the results from the two techniques available for this study will, with practical experience, supplemented by careful thought, provide information that is not available from any other source.

A visual examination of all the Egyptian Blue pellets from the different archaeological sites used in this study demonstrates that the pellets obtained from the 2002 excavation at Fishbourne Roman Palace were of a different standard and quality to those found at Piddington Roma Villa, Turners Hall Farm and Verulamium, even though the LA-ICP-MS and SEM-EDAX analyses shows some similarities. Especially notable were the two friable pellets, FBE02 1071/71421(a) and FBE02 1139/17363), which were almost certainly brought to what was the Fishbourne building site by a skilled master painter who had probably been taught in a school of highly trained professionals on the continent. In addition to Egyptian Blue he would almost certainly also have brought with him the most commonly used ochres, and other common pigments, called the *colores austeri* by Pliny, as well more expensive pigments, which Pliny named the *colores floridi*, the latter normally being provided by the patron at his own expense. One such expensive pigment is the mineral azurite obtained

from Armenia, which, according to Pliny, cost ...*300 sesterces per pound* (Pliny, Book XXXV, XXVIII) and which would have been used exclusively in the production of a vignette.

The ingredients necessary for making Egyptian Blue pellets in Roman Britain would have been readily available during the construction of Fishbourne Roman Palace, Piddington Roman Villa and Turners Hall Farm. During the excavation of Fishbourne Roman Palace evidence has been found of base foundations of Belgic type kilns which may suggest that, with all the different professional skills that were required to build such a grand structure, at least some of the pellets may have been produced locally, on site, using scrap metal obtained from nearby metal-working workshops. Workshops have also been found near the Villa at Turners Hall Farm. The master craftsmen would have instructed the apprentices on the art of manufacturing Egyptian Blue pellets; possibly this would in time have resulted in the local production of pellets.

There is some textural evidence that may be deduced from the analytical data to suggest that pellets from different periods of the Roman occupation have different provenances – early ones (such as the two friable pellets found during the Fishbourne 2002 excavation, *viz.* FBE02 1071/71421(a) and FBE02 1139/17363) are likely to have imported, whereas later ones such as those found in Piddington, Turners Hall Farm and Verulamium, discussed in Chapters 5, 6 and 7 respectively, were probably made locally.

The geochemical data suggests that the Egyptian Blue pellets found at Piddington Roman Villa, Turners Hall Farm and Verulamium, with the exception of Verulamium One, are comparable in that they have a similar

texture, structure and fabric. Looking at the pellets visually and microscopically it is possible to suggest that the occupiers of the high status town houses and villas at Verulamium, and the inhabitants of Turners Hall Farm, employed the same group of artists and their entourage to decorate the internal walls of their houses and villas, as had decorated the interior of Piddington Roman Villa. Another possibility is that one of the wealthy occupiers of a richly decorated town house in Verulamium may have also owned the villa found on Turners Hall Farm and would, therefore, have been likely to have employed the same master craftsmen to decorate the internal walls of that building. In other words it may be suggested that all these pellets had been made by the same group or school of painters (Cunliffe, 1998) who, with their apprentices, travelled to different towns and to large country estates vying for business in order to apply their expertise in the decoration of the interior of high status buildings. As mentioned, the texture, structure and the size of the grains of the pellets from these three sites (*ie* Turners Hall Farm, Piddington and Verulamium) are similar, with the Verulamium One pellet being the single exception; the difference being that the Verulamium One pellet has larger grain sizes and its crystal structure appears cleaned and sorted suggesting that it was made by an expert (see figure 7.4a, page 173).

The pellets found at Piddington Roman Villa, Turners Hall Farm and those provided by Verulamium Museum were all discovered in unique locations: 10 of the Piddington pellets were found in a midden area dated to the late third century whilst the eleventh was found in a feature gully underlying a late first century villa; the three pellets found at Turners Hall Farm were found at three different sites, all being somewhat near workshops; the two Verulamium pellets are museum specimens whose

find location is unknown, but thought to originate from Wheeler's 1930s excavation. As the evidence presented in Chapters 5, 6 and 7 demonstrates the visual and microscopic appearance of the pellets from the three sites (with the exception of the Verulamium One pellet) suggests that all these pellets have a similar texture, structure and fabric. The crystal structure of the pellets from Piddington essentially show an amorphous agglomeration in which only a few defined crystal habits can be identified; the crystal structure of Verulamium Two similarly shows that of an amorphous mass with few identifiable crystal habits. By contrast the three pellets of Turners Hall Farm show different crystal forms which although fractured are readily identifiable. With the exception of one washed grain from Turners Hall Farm (pellet HYP04 043/25) the grains of all the other pellets thus examined have the appearance of being 'unwashed' and were possibly made by apprentices attached to the artisan.

The grain structure of the pellets from Fishbourne Roman Palace also shows that some of the grains had been washed and others had not, examples of washed pellets are FBE02 1071/17421(a) and FBE02 1139/17463. This suggests that the Fishbourne pellets were made by, at least, two different groups of people.

Although attempts to produce the Egyptian Blue pellets under laboratory conditions were successful, it is very difficult to compare and contrast their different firing times with those of the Romano-British Egyptian Blue pellets. Looking at FRP Type II pellet FBE02 1071/17421(a) (page 102) and the modern day, laboratory produced pellet, figure 9.6 (page 212), fired for a total of 144 hours, a comparison of their colours would suggest that the Fishbourne pellet was also fired for long period of time.

The visual data of some of the pellets from Piddington Roman Villa, [*eg* figure 5.7(f) BM089 NN/29, 5.7(i) BM127 VV/15], Verulamium One (figure 7.6a), the laboratory produced pellet (figure 9.3) and the pellet fired in a simulated Belgic kiln (figure 9.26) would suggest that the Romano-British pellets could have firing times which varied from 90 minutes to 24 hours. However, as discussed above (page 204), because of the large number of possible variables involved in the selection and preparation of ingredients, and also in the production process itself, it is not possible to correlate the colour or crystal structure of ancient Egyptian Blue pigments with a firing time. Furthermore, the exposure of ancient pellets to weathering and chemical degradation over the centuries renders the idea of any such correlation unachievable.

By way of contrast it is important to note that since the whole of the production process, from selection and preparation of ingredients to the number and duration of firing times, of laboratory produced Egyptian Blue pigments, is meticulously recorded, a correlation between crystal structure, firing times and the final colour of the pigments can be readily established.

A further considerable factor to note is that both the main analytical techniques used in this study were restricted to surface and near-surface analysis of the structure of the pellets. The constraint imposed upon the author to maintain the integrity of the supplied pellets has meant that they have not been sectioned, nor the internal fabric analysed; it has not been possible, therefore, to confirm that surface and near surface features, which have been studied at length, are reproduced throughout the internal structure of the pellet.

Experiments reproducing Egyptian Blue pellets, both in a controlled laboratory environment and in the field situation, showed mixed success. The field experiments have shown that Egyptian Blue is difficult to make, particularly when using recreated ancient technologies and there are questions still to be answered. There is very little written evidence to indicate how these pellets were manufactured in ancient times. Petrie's discovery of a 'factory' site in Tel el Amarna, gives clues on how Egyptian Blue was produced in Egypt. Vitruvius gives an insight as to how the ingredients, but not the amounts, reacted with each other. Vestorius, it appears, perfected the technique, but did not commit it to a written record. Future work should include more experiments conducted in field studies to address these questions. Especially important is the determination of the length of firing times used when producing these pellets.

Laboratory based investigations have generally proved more positive than those conducted in the field. The determination of the fabric, texture and geochemical structure of the Egyptian Blue pellets was an interesting and worthwhile project that increases our knowledge of the composition and formulation of one the pigments used in decoration of the dwellings of the Romano-British élite. The possible discovery that minerals such as azurite and malachite were used as a pigment in fragments painted wall-plaster found at Verulamium also proved interesting.

The results of this study of Egyptian Blue pellets from different Romano-British sites suggests that the craftsmen did not use a standard recipe when producing the pigment; with few exceptions, the pellets were likely

to have been produced by individual manufacturers and artisans who used the various materials that were available locally at the time of production; this resulted in the production of pellets demonstrating a variety of different blue shades and textures and showing a different geochemical composition.

Other pigments, such as the expensive copper bearing minerals, malachite and azurite, could have been specially purchased and may have been obtained from one of the mines associated with Alderley Edge in Cheshire (Catling, *id.*). Evidence, from SEM-EDAX analysis, suggests that these two minerals (azurite and malachite) were used in the interior decoration of a high status town house found in Verulamium Park. These minerals were probably obtained locally although, according to Pliny, the most expensive azurite was obtained from Armenia (Pliny, Book XXXV, XXVIII). As an alternative to the use of ochres, locally produced Egyptian Blue pellets could also be manufactured on site and would have been much cheaper to purchase than *Vestorian Blue*, the finest Egyptian Blue, which would ...*cost 11 denarii per pound*... (Pliny, Book XXXIII, LVII). Egyptian Blue pellets could be made cheaply from discarded pieces of scrap metal, or they could become a more expensive product when using copper filings or malachite. It is likely that the latter would have been used sparingly, normally only used in the production of a vignette, whereas the cheaper pellets would have been used to cover a whole wall as a background colour in a wall painting.

The specific objectives established as this study was initiated have largely been fulfilled. Experimental work undertaken in field studies has demonstrated how difficult it is, when using simulated ancient technologies, to emulate the skills of the artisans working at Romano-

British sites and elsewhere in the empire. It is evident that using these initial studies as a starting point much further work, time and effort should be undertaken before it would be possible to begin to emulate the techniques, skills and professionalism of the ancient artisans, both in producing what is thought to be the first synthetic pigment, Egyptian Blue - a significant and notable achievement - and in subsequently applying it to the walls of the dwellings of the wealthy Romano-British. The skill of the artisans to produce such a variety of different shades of blue when applying their various skills to the most detailed of paintings is exemplary. A fine example of their craftsmanship, using a variety of blue pigments and techniques, is to be seen in the Villa Oplontis at Naples, shown in figure 10.1

If it were possible to undertake further work on the Egyptian Blue pellets used in this study then it would be worth considering the use of XRF which is claimed to have detection levels at the 1-10 ppm by weight level. Similar or even better results can be obtained from micro-PIXE (Particle-induced X-ray Emission) analyses (Kuisma-Kursula, 1999). Both techniques are non-destructive and can be used to determine the distribution of trace elements in a wide range of archaeological samples; unfortunately neither was available at Sussex University.

Further geochemical work would also need be undertaken, using (modern) LA-ICP-MS technology, in order to try and ascertain where the ancient artist obtained copper, one of the main ingredients used in the manufacture of some of the Egyptian Blue pellets. It is hoped that it will be possible to do this by identifying copper isotopes and thereby trace national and international trade routes so that it may be possible to establish whether the copper was sourced locally or imported.

The poet Horace (65-68 BC) informs us that the Greeks ...*once*... [they had] *overcome* [their] *wild conqueror[s]* ...*brought the arts into rustic Latium*... Subsequently, through their newly acquired technical expertise, the ‘rustic’ Roman conquerors brought the art of interior decoration to these so-called ‘uncivilised’ shores.



Figure10.1 Shrine dedicated to the god Apollo, the receiving room, Villa Oplontis, Naples, Italy.

(Picture taken by the author)

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Appendix A:

The Munsell Color Reference System

The Munsell Book of Color

The Munsell numbers used in this text to identify the colours of different archaeological specimens are of that system first described by A H Munsell in 1915 and now available in the *Munsell Book of Color (Matte Finish Collection)* 2001. The system identifies colour in terms of three attributes: hue (H), value (V) and chroma (C); the identification being specified by a code in the symbolic form: *H V/C*. Hue is based on ten major standards arranged in a circular scale. *viz.* Red, Yellow-Red, Yellow, Yellow-Green, Green, Blue-Green, Blue, Purple-Blue, Purple and Purple-Red. In total the Munsell collection contains a 100 equally spaced hues arranged on a 100 hue circuit surrounding the neutral spine. For computing and statistical purposes the hue circuit may be represented entirely numerically but for normal descriptive purposes, however, the hue notation consists of a number and a letter, such as 2.5 YR (signifying 2.5 Yellow-Red).

The value notation indicates the degree of lightness of the colour in relation to a neutral grey scale which extends from absolute black, represented as 0/, to absolute white, represented as 10/. The chroma (or saturation) notation indicates the degree of departure of a given hue from a neutral grey of the same value (lightness). A neutral value scale graded in equal visual steps from black at the bottom to white at the top forms the central core or axis of the system. By use of a decimal system each scale [H, V and C] may be divided into increments as small as required for accurate colour identification. As an example of the application of the Munsell notation, the colour commonly described as 'rose' might be classified as 5R 5/4 in this system.

Although under ideal conditions the human eye can perceive several million different colours, it is economically impractical to produce a vast number of coloured samples for use as comparators. The Munsell matte atlas displays 1185 colour standards permanently mounted on loose-leaf charts for 40 different hues.

The Munsell colour system has gained world-wide acceptance as a standard reference work in those fields for which colour identification is important. Many British colour standards are expressed in terms of the Munsell system.

All significant colour observations should be made under standard conditions of illumination. It is suggested that the observer should view the sample and the standards at 90° and that the light should fall upon them at about 45° . Clearly, those working and making decisions in the field of colour should previously have been examined for possible colour vision defects, for instance by examination of Ishihara charts.

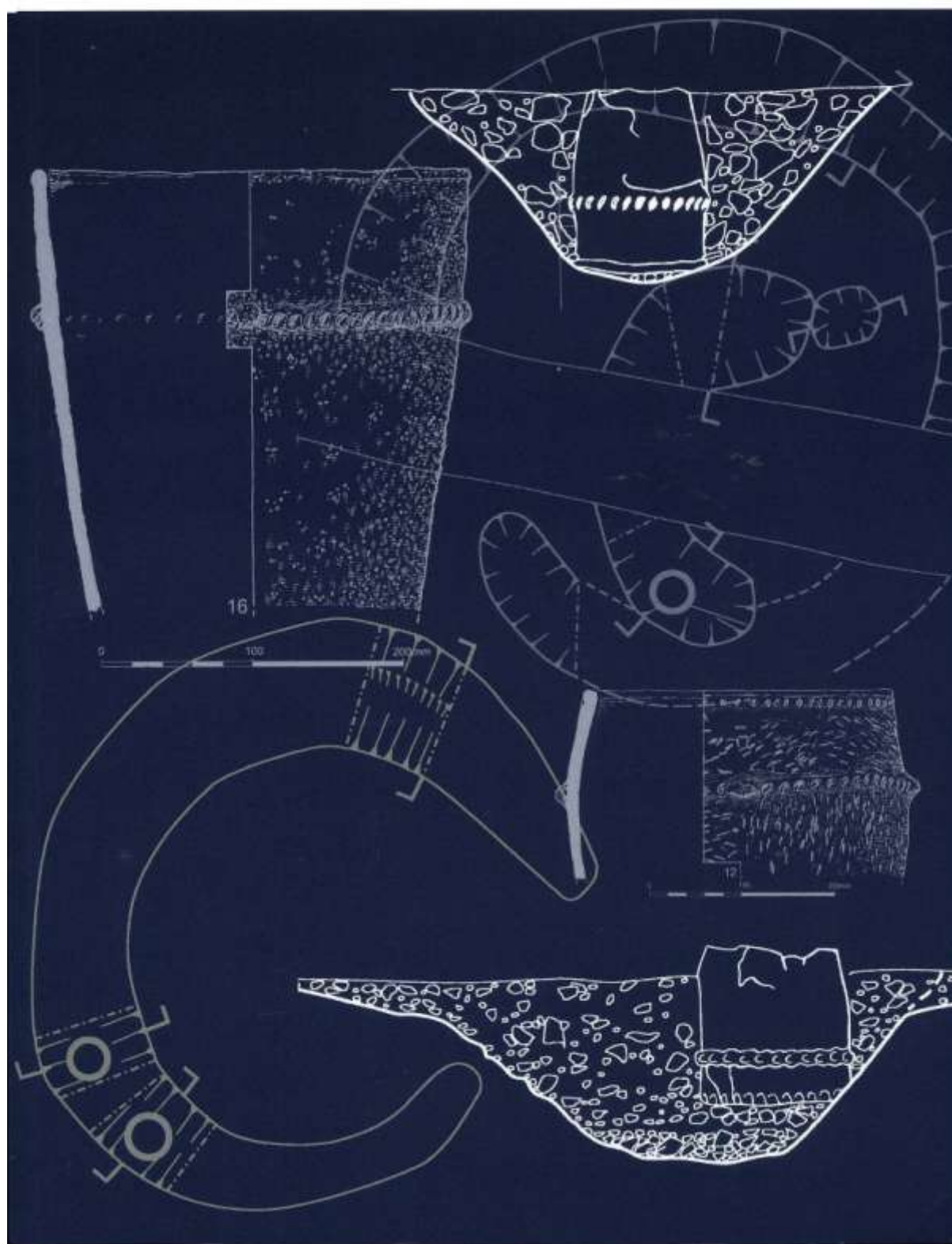
Ideally the specimen to be examined should be of uniform colour and gloss and free from scratches, brush marks and other imperfections in the surface texture. Archaeological specimens are often not of a single or uniform colour and are seldom free of imperfections: the matching of colours is thus likely to be, in most cases, somewhat artificial. Nevertheless, use of the Munsell system may provide a guide and an aid to the comparison of disparate specimens.

Appendix B:

Paper published by the author

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Relating to the history and antiquities
of the counties of East and West Sussex

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BLUE FRIT

by Sue Clegg, Andrew Cundy & Christopher Dadswell
This report presents preliminary textural and geochemical data for the blue pellets recovered from Fishbourne Roman Palace during excavations in 2002. The pellets were examined by Laser Ablation Inductively Coupled Plasma Mass Spectrometer (LA-ICP-MS) and by Stereomicroscopy in order to (a) qualitatively determine their chemical composition, fabric and texture, and (b) attempt a preliminary textural (and geochemical) classification.

Background: blue frit

Materials and methods

On the ADS website are photographs, together with a magnified view, of the pellets found in various contexts at Fishbourne Roman Palace during the excavation season of 2002. Beneath each photograph is a printout of the LA-ICP-MS results obtained for each of the pellets.

Results

The texture and structure of all twelve of the pellets was closely examined by the naked eye and also microscopically. As a result of this examination they were divided into four types, conveniently labelled as Fishbourne Roman Palace (FRP) Types I, II, III and IV (Table 2).

The structure of FRP Type I shows that the ingredients of the pellets had been roughly ground. The quartz grains are large and there are few inclusions. The composition of FRP Type II pellets is very different: the ingredients of these pellets have been finely ground, and there are some small inclusions. The quartz grains are also smaller in size. FRP Type III pellets varied slightly from those of Types I and II: although the ingredients of these pellets had been finely ground there were a few large grains of quartz, but very few inclusions. The ingredients of FRP Type IV pellets had been finely ground and there are no inclusions.

Table 2. Blue frit pellet fabric and structure types: relation to the chemical composition groups.

| Group | Context/Sample ID |
|--------------|--|
| FRP Type I | FBE02 1145/173632 (a); FBE02 1010/14932; FBE02 1013/14376 |
| FRP Type II | FBE02 1139/17463; FBE02 1071/17421 (a); FBE02 1071/17421 (b); FBE02 1005/14448 |
| FRP Type III | FBE02 1024/15353; FBE02 1029/16203; FBE02 1006/16512 |
| FRP Type IV | FBE02 1005/14174; FBE02 1005/14454 |

Chemical analysis of the pellets by LA-ICP-MS shows significant variation in the amounts of copper, iron, silica, barium, tin and lead found in the individual pellets.

These variations, while based on qualitative, rather than quantitative LA-ICP-MS scans, indicate considerable heterogeneity in either the material sourced to produce these pellets, or in the mixture of the ingredients. The presence of above-background levels of tin and lead, alongside copper, is common to all but one of the samples, raising the possibility that scrap metal, in particular bronze scrap, was an important ingredient in the production of the pellets. Further work to quantify these geochemical variations is under way.

Discussion and conclusion

The results of this study suggest that the Romans did not use a standard recipe when producing blue frit and that the pellets were most probably produced by individual manufacturers who used the various materials that were available at the time of production; this resulted in the production of a variety of differing shades and textures of blue pellets (with different geochemical composition). Cost may also have come into consideration. According to Damiani *et al.* (2003), blue frit pellets could be made cheaply from discarded pieces of scrap metal, or they could become an expensive product when using copper filings or malachite. It is likely that the latter would have been used sparingly as part of a vignette whereas the cheaper pellets would have been used to cover a whole wall as a background colour in a wall painting.

The ingredients for making blue frit would have been readily available during the construction of Fishbourne Roman Palace. During the excavation of the Palace evidence of base foundations of Belgic-type kilns have been found which may suggest that, with all the different professional skills that were required to build such a grand structure, at least some of the pellets may have been produced locally on site. On the other hand the ancient artisan would have brought the tools of his trade, and samples of blue frit pellets, with him.

A detailed examination of the three blue frit pellets (FBE02 1071/17421 [a and b] and FBE02 1139/17363), classified as FRP Type II, Table 2, are quite friable to touch and different in texture and structure from all the other pellets

found during the excavation. They were found in a very early ditch predating AD 43. During the excavation the bottom of the ditch was moist and owing to the clayey condition of the soils, small objects could easily have become attached to the soles of footwear. It has been suggested that the location of these pellets, found in the excavated ditch, could be the result of contamination. Reference to the date of these finds should, therefore, be treated with caution since painted plaster from this early date is very rare (Clegg, 2005).

The FRP Type II blue pellet, FBE02 1005/14448, is of a similar composition to the three Type II pellets mentioned above, but unlike them, is not friable to touch.

Dr W. J. Russell (1892) who wrote a paper on colours from the Egyptian site of Medum, which was excavated during the late 1890s by Sir Flinders Petrie, said after examining a large number of blue frit pellets that '... every specimen of the frits that I have seen has been in the friable condition ... [and] ... on rubbing they can be readily reduced to powder.' (p 46: 5 11) The three friable Type II pellets from Fishbourne

were most probably made by a specialist and may have been manufactured at (and imported from) a factory site, such as that found at the Campanian city of Puteoli (Forbes 1955). They may have been brought to Fishbourne Roman Palace by a master-craftsman. These three friable pellets could have been samples of a larger batch used to decorate parts of the interior walls of Fishbourne Roman Palace during its initial construction. There is some textural evidence that pellets of different periods have different sources — early ones are imported, later ones are local.

The skill of the ancient craftsmen in developing one of the first synthetic pigments has to be admired especially for producing such a variety of different shades of blue. The poet Horace (65–8 BC) informs us that 'the Greeks ... once ... [they had] overc[ame] [their] wild conqueror[s] ... brought the arts into rustic Latium'.¹⁵ Subsequently, through their newly acquired technical expertise, the 'rustic' Roman conquerors brought the art of interior decoration to these so-called 'uncivilised' shores.